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Selected Processes

IT Enviroscience
Knoxville, TN

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EPA is developing new source performance standards under Section 111 of the Clean Air Act and national emission standards for hazardous air pollutants under Section 112 for volatile organic compound emissions (VOC) from organic chemical manufacturing facilities. In support of this effort, data were gathered on chemical processing routes, VOC emissions, control techniques, control costs, and environmental impacts resulting from control. These data have been analyzed and assimilated into the ten volumes comprising this report.

This volume presents in-depth studies of several major organic chemical products.

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Volume 6: Selected Processes

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

December 1980

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INTRODUCTION

A. SOCMI PROGRAM

Concern over widespread violation of the national ambient air quality standard for ozone (formerly photochemical oxidants) and over the presence of a number of toxic and potentially toxic chemicals in the atmosphere led the Environmental Protection Agency to initiate standards development programs for the control of volatile organic compound (VOC) emissions. The program goals were to reduce emissions through three mechanisms: (1) publication of Control Techniques Guidelines to be used by state and local air pollution control agencies in developing and revising regulations for existing sources; (2) promulgation of New Source Performance Standards according to Section 111(b) of the Clean Air Act; and (3) promulgation, as appropriate, of National Emission Standards for Hazardous Air Pollutants under Section 112 of the Clean Air Act. Most of the effort was to center on the development of New Source Performance Standards.

One program in particular focused on the synthetic organic chemical manufacturing industry (SOCMI), that is, the industry consisting of those facilities primarily producing basic and intermediate organics from petroleum feedstock meterials. The potentially broad program scope was reduced by concentrating on the production of the nearly 400 higher volume, higher volatility chemicals estimated to account for a great majority of overall industry emissions. EPA anticipated developing generic regulations, applicable across chemical and process lines, since it would be practically impossible to develop separate regulations for 400 chemicals within a reasonable time frame.

To handle the considerable task of gathering, assembling, and analyzing data to support standards for this diverse and complex industry, EPA solicited the technical assistance of IT Enviroscience, Inc., of Knoxville, Tennessee (EPA Contract No. 68-02-2577). IT Enviroscience was asked to investigate emissions and emission controls for a wide range of important organic chemicals. Their efforts focused on the four major chemical plant emission areas: process vents, storage tanks, fugitive sources, and secondary sources (i.e., liquid, solid, and aqueous waste treatment facilities that can emit VOC).

B. REPORTS

To develop reasonable support for regulations, IT Enviroscience gathered data on about 150 major chemicals and studied in-depth the manufacture of about 40 chemical products and product families. These chemicals were chosen considering their total VOC emissions from production, the potential toxicity of emissions, and to encompass the significant unit processes and operations used by the industry. From the in-depth studies and related investigations, IT Enviroscience prepared 53 individual reports that were assembled into 10 volumes. These ten volumes are listed below:

Volume I : Study Summary
Volume II : Process Sources
Volume III : Storage, Fugitive, and Secondary Sources
Volume IV : Combustion Control Devices
Volume V : Adsorption, Condensation, and Absorption Devices
Volume VI-X: Selected Processes

This volume is a compilation of individual reports for the following chemical products: cyclohexane, cyclohexanol, cyclohexanone, chlorobenzenes, maleic anhydride, ethylbenzene, styrene, caprolactam, adipic acid. The reports generally describe processes used to make the products, VOC emissions from the processes, available emission controls, and the costs and impacts of those controls (except that abbreviated reports do not contain control costs and impacts). Information is included on all four emission areas; however, the emphasis is on process vents. Storage tanks, fugitive sources, and secondary sources are covered in greater detail in Volume III. The focus of the reports is on control of new sources rather than on existing sources in keeping with the main program objective of developing new source performance standards for the industry. The reports do not outline regulations and are not intended for that purpose, but they do provide a data base for regulation development by EPA.

C. MODEL PLANTS

To facilitate emission control analyses, the reports introduce the concept of a "model plant" (not in abbreviated reports). A model plant by definition is a representation of a typical modern process for production of a particular chemical. Because of multiple production routes or wide ranges in typical production capacities, several model plants may be presented in one product report. The model plants can be used to predict emission characteristics of a new plant. Of course, describing exactly what a new plant will be like is difficult because variations of established production routes are often practiced by individual companies. Nonetheless, model plants provide bases for making new-plant emission estimates (uncontrolled and controlled), for selecting and sizing controls for new plants, and for estimating cost and environmental impacts. It is stressed that model-plant analyses are geared to new plants and therefore do not necessarily reflect existing plant situations.

REPORT 1

CYCLOHEXANE

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Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

September 1980

This report contains certain information which has been extracted from the Chemical Economics Handbook, Stanford Research Institute. Wherever used, it has been so noted. The proprietary data rights, which reside with Stanford Research Institute, must be recognized with any use of this material.

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Cyclohexane production was selected for study because preliminary estimates indicated that product growth rates and volatile organic compound (VOC) emissions would be high. In addition cyclohexane manufacture was of special interest because benzene is commonly used as a feedstock. Cyclohexane and benzene, the two major organic components in cyclohexane manufacture, are both colorless liquids; their pertinent physical properties are given in Appendix A.

B. USAGE AND GROWTH

Cyclohexane is the first intermediate in a series of chemicals that leads to the production of nylon 6,6 and nylon 6; the intermediates and their relationships to cyclohexane are shown in Fig. II-1. Table II-1 shows cyclohexane end uses and expected growth rates.

The annual growth rate of cyclohexane production by the benzene hydrogenation process is reported to be 6 to 6 1/2%.[1] Production by the petroleum separation process is expected to decrease annually by 1 1/2%.[2] if an overall cyclohexane production growth rate of 5%/yr occurs, as expected, for the period 1976 to 1982.

The 1977 domestic cyclohexane production capacity was reported to be 1395 gigagrams (Gg); 71% of the capacity was utilized.[1] Based on an overall growth rate of 5%, over 90% of the domestic capacity will be utilized by 1982.

C. DOMESTIC PRODUCERS

In the late 1960s, 17 producers of cyclohexane in the United States (including Puerto Rico) shared a market of only a few large customers. Competition forced a number of the producers to close their plants, and today only 9 producers with 11 plants produce cyclohexane.[1] Table II-2 gives the producers, along with the estimated capacities and the process used; Fig. II-2 shows the manufacturing locations.

The availability of low-cost, high-purity hydrogen is a prerequisite for cyclohexane production by either process. Consequently, all cyclohexane production

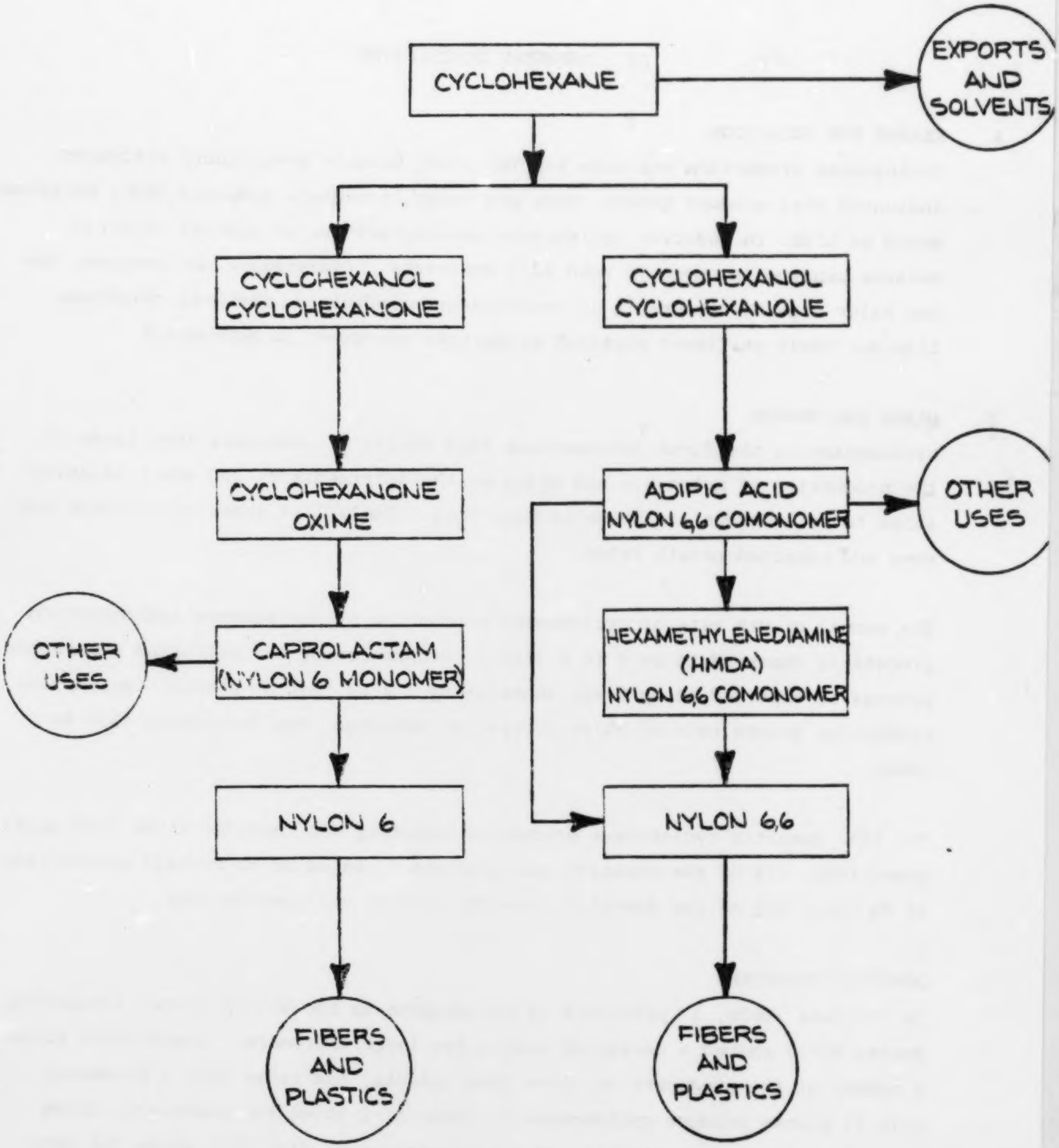

CYCLOHEXANE
EXPORTS AND SOLVENTS
CYCLOHEXANOL CYCLOHEXANONE
CYCLOHEXANOL CYCLOHEXANONE
CYCLOHEXANONE OXIME
ADIPIC ACID NYLON 6,6 COMONOMER
OTHER USES
CAPROLACTAM (NYLON 6 MONOMER)
OTHER USES
HEXAMETHYLENEDIAMINE (HMDA) NYLON 6,6 COMONOMER
NYLON 6
NYLON 6,6
FIBERS AND PLASTICS
FIBERS AND PLASTICS

Fig. II-1. Cyclohexane and Its Relationship to Manufacture of Other Organic Chemicals

Table II-1. Cyclohexane Usage and Growth[a]

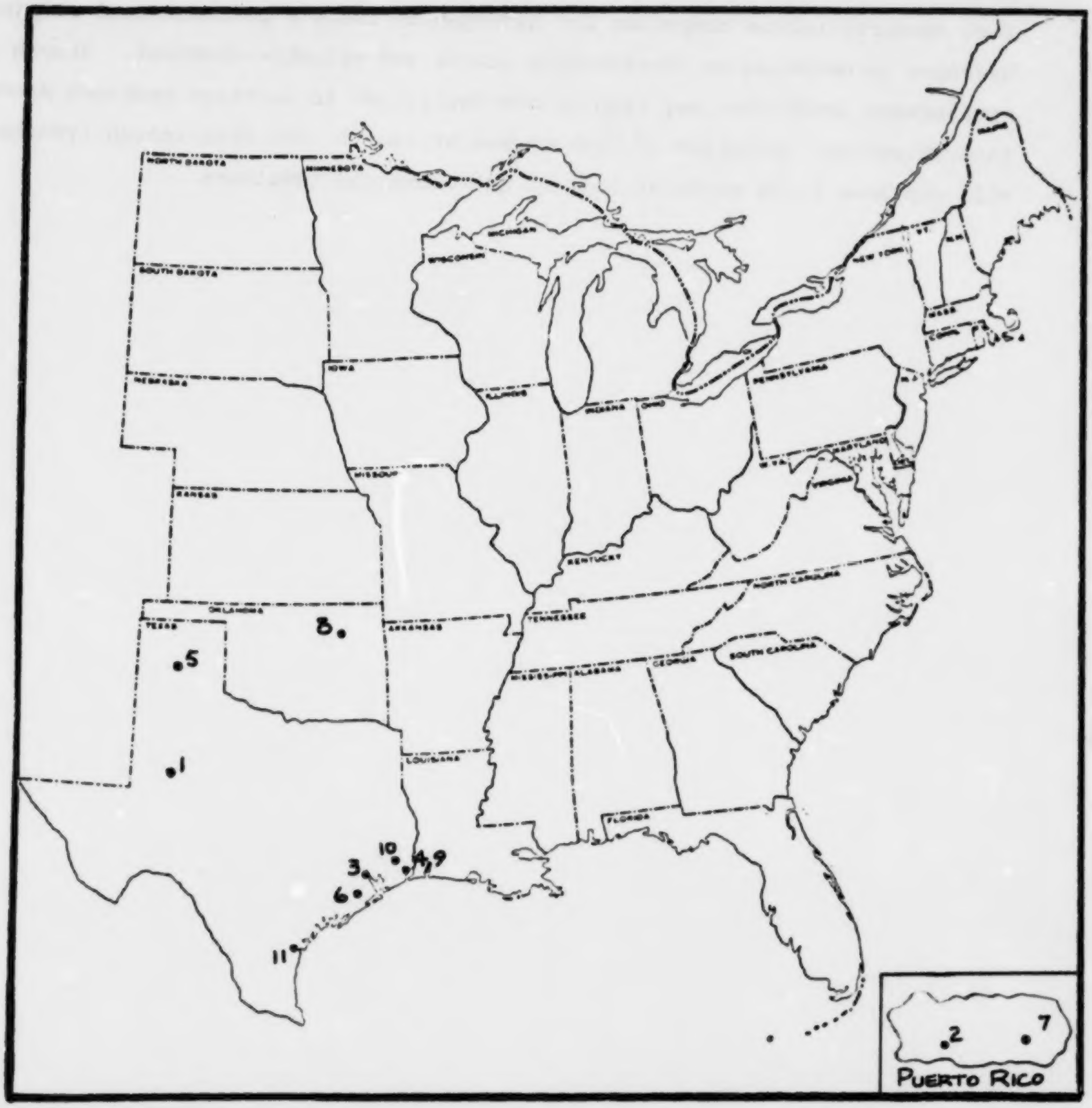
End Use	Percent of Production (1976)	Average Annual Growth (%) (1976-1981)
Adipic acid	53	5.0
Exports	18	
Caprolactam	23	8.5—10.0
1,6-Hexamethylenediamine (HMDA)	3	2.0
Miscellaneous	3	1.5
Average		6.0—6.5

[a] See ref 1.

Table II-2. Cyclohexane Capacity[a]

Producer	Location	1976 Capacity (Gg)	Process
American Petrofina, Inc. Cosden Oil & Chemical Co., sub.	Big Spring, TX	35	b
Commonwealth Oil Refining Co., Inc. Corco Cyclohexane, Inc., sub.	Penuelas, PR	117	b
Exxon Chemical Co., USA Division of Exxon Corp.	Baytown, TX	147	b
Gulf Oil Chemicals Co. Division of Gulf Oil Corp.	Port Arthur, TX	106	b
Phillips Petroleum Co.	Borger, TX	117	c
	Sweeny, TX	250	b,c
Phillips Puerto Rico Core, Inc., sub.	Guayama, PR	212 (expanding to 265)	b
Sun Company, Inc.	Tulsa, OK	59 (expanding to 88)	b
Texaco, Inc.	Port Arthur, TX	117	b
Union Oil of California	Beaumont, TX	88	b
Union Pacific Corp. Champlin Petroleum Co., sub.	Corpus Christi, TX	65	b
Total		1313	
With expansions		1395	

[a] See ref 1.
[b] Benzene hydrogenation.
[c] Petroleum separation.


NORTH DAKOTA
MINNESOTA
SOUTH DAKOTA
WISCONSIN
MICHIGAN
NEW YORK
NEBRASKA
IOWA
ILLINOIS
INDIANA
OHIO
PENNSYLVANIA
KANSAS
MISSOURI
KENTUCKY
NORTH CAROLINA
OKLAHOMA
TEXAS
ARKANSAS
TENNESSEE
SOUTH CAROLINA
MISSISSIPPI
ALABAMA
GEORGIA
LOUISIANA
FLORIDA
8
5
1
10
3
4,9
6
11
2
7
PUERTO RICO

1. Cosden - Big Spring, TX
2. Corco - Penuelas, PR
3. Exxon - Baytown, TX
4. Gulf - Port Arthur, TX
5. Phillips - Borger, TX
6. Phillips - Sweeny, TX
7. Phillips - Guayama, PR
8. Sun - Tulsa, OK
9. Texaco - Port Arthur, TX
10. Union Oil - Beaumont, TX
11. Champlin - Corpus Christi, TX

Fig. II-2. Locations of Plants Manufacturing Cyclohexane

plants are located in petrochemical complexes. However, with such processes as fuel desulfurization competing for hydrogen in today's petrochemical complexes, hydrogen is becoming an increasingly scarce and valuable chemical. Growth in cyclohexane production may require new facilities to increase hydrogen production through partial oxidation of hydrocarbon streams.[2] For this reason cyclohexane will continue to be produced only in petrochemical complexes.

D. REFERENCES*

1. J. L. Blackford, "Cyclohexane," pp 638.5061A, 638.5062W in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (February 1977).

2. R. W. Smith, "What's Happening with Cyclohexane?" Chemical Engineering Progress 73(9), 25—28 (1977).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTIONS

A. INTRODUCTION

Two processes are used commercially to manufacture cyclohexane: catalytic hydrogenation of benzene, which accounts for approximately 85% of the cyclohexane capacity in the United States; and separation from petroleum liquids, which constitutes the remaining 15%.

B. CYCLOHEXANE PRODUCTION BY HYDROGENATION OF BENZENE

1. Basic Process

The reaction utilized to make cyclohexane from benzene is:

$$\underset{\text{(benzene)}}{C_6H_6} + \underset{\text{(hydrogen)}}{3H_2} \longrightarrow \underset{\text{(cyclohexane)}}{C_6H_{12}}$$

Figure III-1 shows a model-plant* flow diagram for the manufacture of cyclohexane by benzene hydrogenation. High-purity benzene is stored in large tanks near the production plant. Benzene (stream 1) is fed to the reactors in parallel, whereas hydrogen (stream 5) is fed into the reactors in series. Part of the cyclohexane separated in the flash separator is recycled (stream 3) and fed to the reactors in series. Recycling helps to control the reactor temperature, since the reaction is highly exothermic. Typical temperatures and pressures in the reaction section are 150 to 260°C and 2.1 to 3.5 MPa. The temperature is also controlled by generating steam, which is used elsewhere in the petrochemical complex. Both platinum and nickel catalysts are presently used to produce cyclohexane.

The cyclohexane (stream 9) leaving the flash separator is sent to a distillation column (stabilizer) for removal of methane, ethane, other light hydrocarbons, and soluble hydrogen gas from the cyclohexane product. These impurities (stream 10) are routed to the complex-wide fuel-gas storage system and used as fuel in process heaters. Flow of this stream for one manufacturer is reported to be 0.018 kg of gas/kg of cyclohexane produced at capacity. Composition is reported to be 42.2 mole % H_2, 44.7 mole % single-carbon compounds, 11.9 mole %

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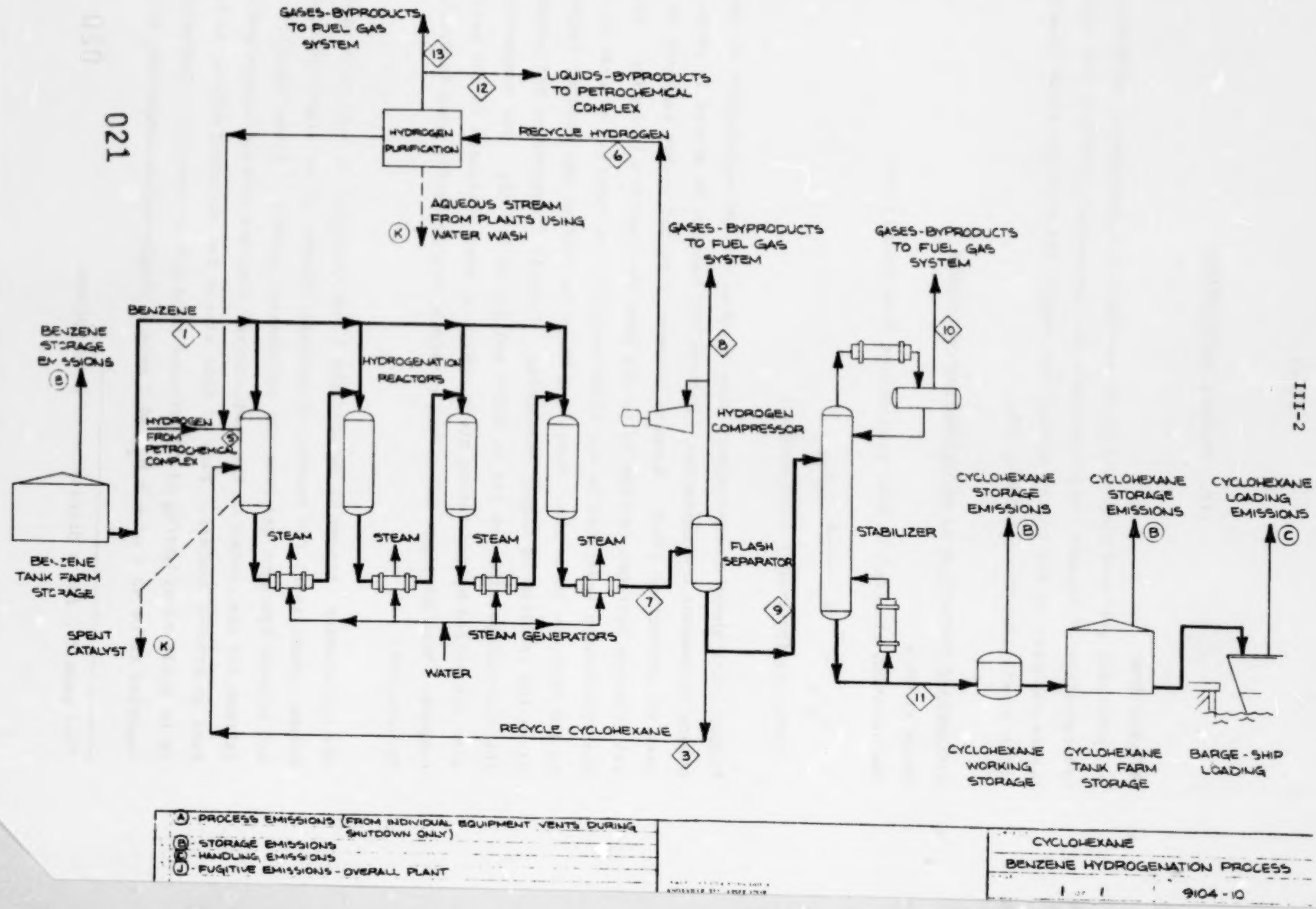
*See page I-2 for a discussion of model plants.

Fig. III-1. Process Flow Diagram for Benzene Hydrogenation Process Model Plant (Uncontrolled Emissions)


GASES-BYPRODUCTS TO FUEL GAS SYSTEM
13
12
LIQUIDS-BYPRODUCTS TO PETROCHEMICAL COMPLEX
HYDROGEN PURIFICATION
RECYCLE HYDROGEN
6
AQUEOUS STREAM FROM PLANTS USING WATER WASH
K
GASES-BYPRODUCTS TO FUEL GAS SYSTEM
GASES-BYPRODUCTS TO FUEL GAS SYSTEM
BENZENE
1
BENZENE STORAGE EMISSIONS
B
8
10
HYDROGENATION REACTORS
HYDROGEN FROM PETROCHEMICAL COMPLEX
5
HYDROGEN COMPRESSOR
CYCLOHEXANE STORAGE EMISSIONS
B
CYCLOHEXANE STORAGE EMISSIONS
B
CYCLOHEXANE LOADING EMISSIONS
C
STEAM
STEAM
STEAM
STEAM
FLASH SEPARATOR
STABILIZER
BENZENE TANK FARM STORAGE
7
9
SPENT CATALYST
K
STEAM GENERATORS
WATER
11
RECYCLE CYCLOHEXANE
3
CYCLOHEXANE WORKING STORAGE
CYCLOHEXANE TANK FARM STORAGE
BARGE-SHIP LOADING
A - PROCESS EMISSIONS (FROM INDIVIDUAL EQUIPMENT VENTS DURING SHUTDOWN ONLY)
B - STORAGE EMISSIONS
C - HANDLING EMISSIONS
J - FUGITIVE EMISSIONS - OVERALL PLANT
CYCLOHEXANE
BENZENE HYDROGENATION PROCESS
1 of 1
9104-10

two-carbon compounds, with the remainder being oxygen, argon, and nitrogen.[1] Cyclohexane (stream 11) purified in the stabilizer may be greater than 99.9% pure.[2,3] The residual benzene content is typically less than 500 mg/liter.[2] This pure product is stored in large tanks to await shipment.

Gas from the flash separator, largely hydrogen (60 to 80 mole %), is not pure enough for direct reuse. This stream (6) is purified to greater than 90 mole % before being recycled to (stream 5) the reactor. Typical processes used for hydrogen purification are absorption and stripping of the hydrogen gas and cryogenic separation; some plants use a combination of the two processes. Organic liquids (stream 12) separated from the hydrogen in the hydrogen purification unit are sent to other petroleum processing units in the petrochemical complex. The separated gases (stream 13) are used as fuel gas.

Depending on the type of hydrogen purification used, inert impurities present in the gas from the flash separator can be purged from the system before the gas enters the hydrogen purification equipment. This stream (8) is sent to the fuel gas system. One manufacturer reports that the flow of this stream is 0.96 kg of gas/kg of cyclohexane produced at capacity.[1] The composition of the stream is the same as that of stream 10. The flow and composition of stream 8 will vary for each manufacturer because hydrogen may be purified by several different methods.

There are no process emissions during normal operation. During shutdowns individual equipment vents are opened as required during final depressurization of equipment. Except for the feed streams the concentration of benzene in the process equipment is low; therefore little or no benzene emissions would be expected during a shutdown.[1]

Fugitive leaks can emit benzene, cyclohexane, methane, or other hydrocarbons. Leaks from heat exchangers into cooling water or steam production can be a potential fugitive loss. Fugitive losses are of special significance because of the high diffusivity of hydrogen at elevated temperature and pressure and the extremely flammable nature of the liquid and gas processing streams.

Storage emission sources (labeled B on Fig. III-1) include benzene and cyclohexane storage. In plants where absorption is used for hydrogen purification, an additional organic compound (toluene, glycol amine, etc.) may be stored, but the quantities of these solvents are usually small relative to the quantities of benzene and cyclohexane. Handling emissions (C, Fig. III-1) relate to transfer of cyclohexane to shipping vessels.

The potential sources of secondary emissions (K, Fig. III-1) are catalyst handling and absorber wastewater (where an aqueous solution is used to purify the recycled hydrogen). Plants comprising at least 16% of the total cyclohexane capacity use an aqueous solution to purify hydrogen. Caution is taken to remove the organic from the spent catalyst before it is replaced. The spent catalyst is sold for metal recovery.

2. Process Variations

The most significant variation in the cyclohexane process is the type of catalyst used. Present-day plants use either platinum or nickel on an inert support as a catalyst. Operating temperatures and pressures vary in relation to which catalyst is used. Nickel catalysts are poisoned by sulfur compounds; therefore benzene and hydrogen feeds must be sulfur-free. Also, nickel catalysts require monitoring and replacement at more frequent intervals than do platinum catalysts. One manufacturer using a nickel catalyst replaces all the catalyst beds every four years,[3] whereas a manufacturer using a platinum catalyst reports catalyst lifetimes in excess of ten years.[2] Nickel catalysts also require a small supplemental heater to supply high-temperature hydrogen to convert the nickel catalyst from an oxidized form to a reduced form before startup of a new bed.

Other variations in cyclohexane production include the number of reactors, the type of reactor cooling equipment, and the level of process control used. One manufacturer uses steam-driven compressors instead of electrically powered compressors because the local power company is unreliable and plant safety would be threatened unless hydrogen flow were maintained through the reactors. The steam-driven compressor assures that there will be hydrogen flow during power interruption.[3]

C. CYCLOHEXANE PRODUCTION BY SEPARATION FROM PETROLEUM LIQUIDS

The petroleum separation process is used at two sites to produce cyclohexane from petroleum fractions; these sites prouce 15% of the cyclohexane produced domestically. Cyclohexane of low purity can be commercially obtained by conventional distillation; however, the presence of benzene and isomers of cyclohexane (methylcyclopentane, hexanes, etc.) with vapor pressures similar to that of cyclohexane makes the distillation of cyclohexane with purity greater than 85% very difficult. To produce high-purity cyclohexane, additional process steps are incorporated.

Figure III-2 is a flow diagram of the process used to manufacture high-purity (99%) cyclohexane from petroleum streams.[4,5] A petroleum fraction rich in cyclohexane (stream 1) is fed to a distillation column, where benzene and methylcyclopentane are removed (stream 2) and routed to a hydrogenation unit. The bottoms (stream 3) from the column containing cyclohexane and other hydrocarbons are combined with another petroleum stream (4) and sent to a catalytic reformer, where the cyclohexane is converted to benzene. The hydrogen generated in this step (stream 5) is used in the hydrogenation step or elsewhere in the petrochemical complex.

The benzene-rich stream (6) leaving the catalytic reformer is sent to a distillation column, where compounds that have vapor pressures higher than benzene (pentanes, etc.) are removed (stream 7) and used as by-products. The benzene-rich stream (8) that is left is sent to another distillation column, where the benzene and methylcyclopentane (stream 9) are removed. The remaining hydrocarbons (largely dimethylpentanes) are used elsewhere in the petrochemical complex as by-products (stream 10).

Stream 9 (benzene and methylcyclopentane) is combined with stream 2 and sent to a hydrogenation unit similar to the one discussed in the hydrogenation process (Sect.III-B). Hydrogen is fed to this unit, and the benzene is converted to cyclohexane (stream 11). Isomers of cyclohexane such as methylcyclopentane are converted to cyclohexane in an isomerization unit, and the effluent (stream 12) from this equipment is separated in a final distillation step. Pure cyclohexane (stream 14) is separated from isomers of cyclohexane (stream 13) and compounds with lower vapor pressures (stream 15).

Fig. III-2. Process Flow Diagram for Petroleum Separation Process Model Plant (Uncontrolled Emissions), (refs. 4,5)

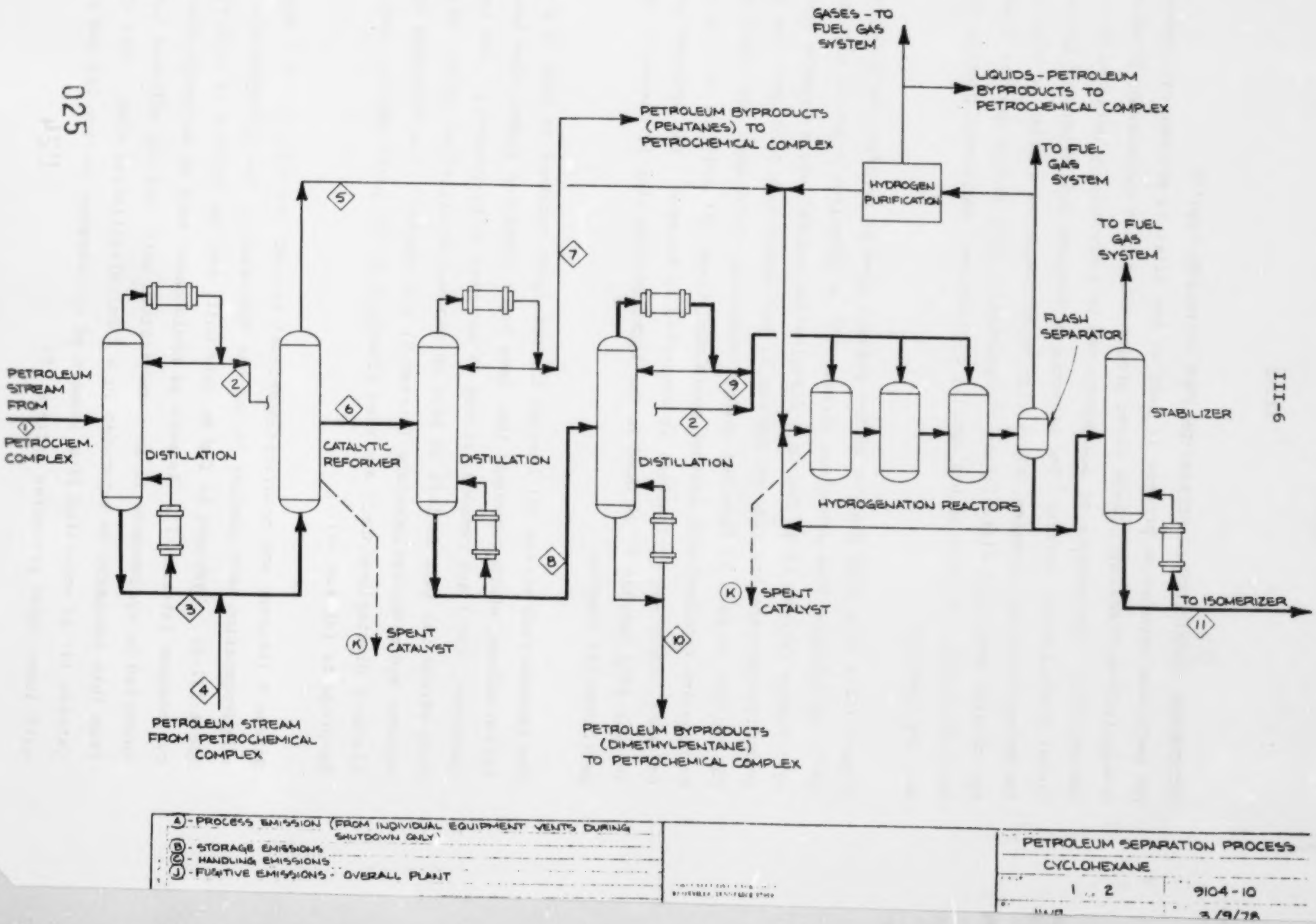
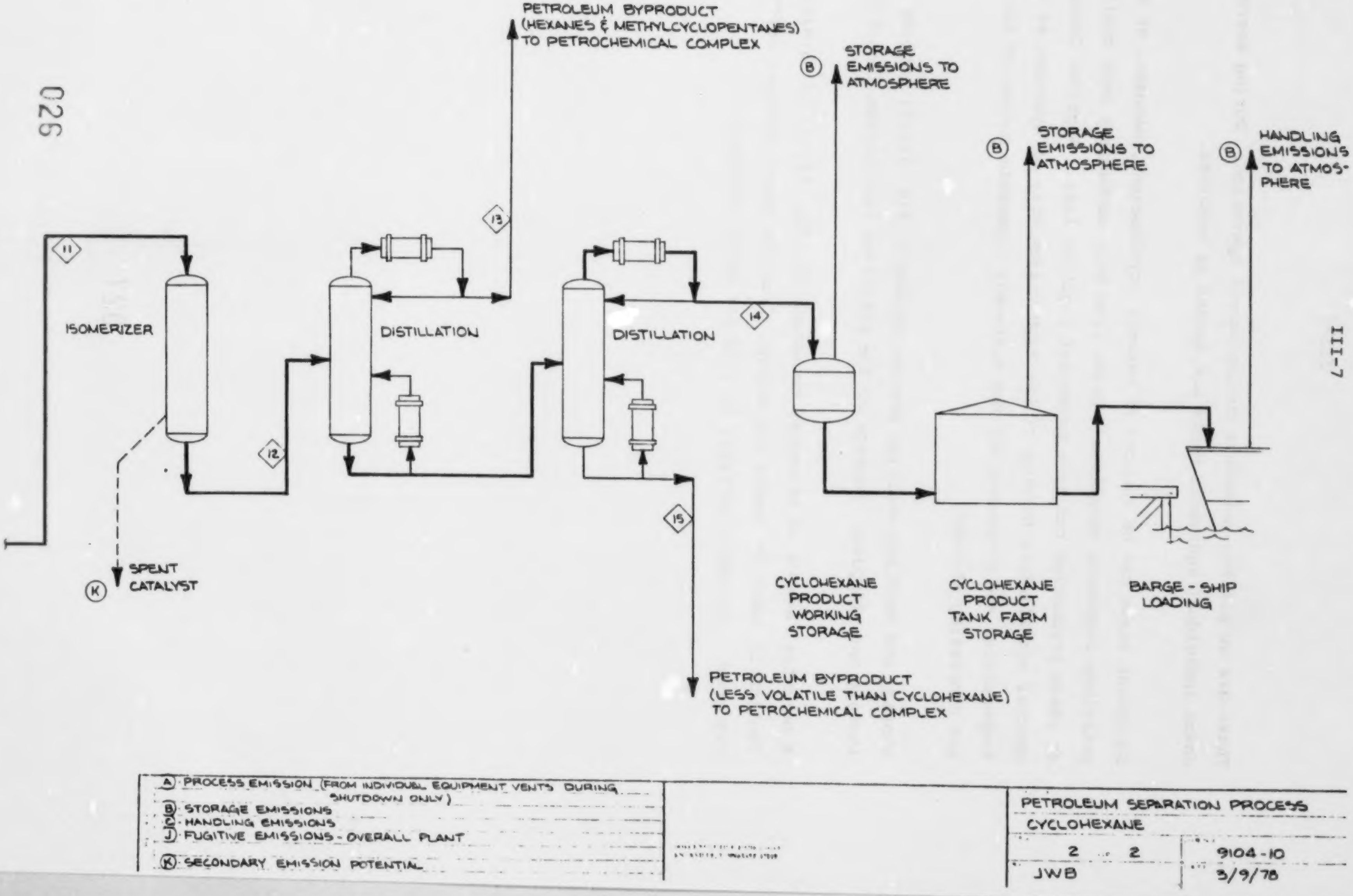

GASES - TO FUEL GAS SYSTEM
LIQUIDS - PETROLEUM BYPRODUCTS TO PETROCHEMICAL COMPLEX
PETROLEUM BYPRODUCTS (PENTANES) TO PETROCHEMICAL COMPLEX
HYDROGEN PURIFICATION
TO FUEL GAS SYSTEM
TO FUEL GAS SYSTEM
FLASH SEPARATOR
PETROLEUM STREAM FROM ① PETROCHEM. COMPLEX
DISTILLATION
CATALYTIC REFORMER
DISTILLATION
DISTILLATION
STABILIZER
HYDROGENATION REACTORS
5
7
2
6
9
2
3
8
K SPENT CATALYST
K SPENT CATALYST
TO ISOMERIZER
11
10
4
PETROLEUM STREAM FROM PETROCHEMICAL COMPLEX
PETROLEUM BYPRODUCTS (DIMETHYLPENTANE) TO PETROCHEMICAL COMPLEX
A - PROCESS EMISSION (FROM INDIVIDUAL EQUIPMENT VENTS DURING SHUTDOWN ONLY)
B - STORAGE EMISSIONS
C - HANDLING EMISSIONS
J - FUGITIVE EMISSIONS - OVERALL PLANT
PETROLEUM SEPARATION PROCESS
CYCLOHEXANE
1 2
9104-10
3/9/78

Fig. III-2. (Continued)


PETROLEUM BYPRODUCT
(HEXANES & METHYLCYCLOPENTANES)
TO PETROCHEMICAL COMPLEX
B
STORAGE EMISSIONS TO ATMOSPHERE
B
STORAGE EMISSIONS TO ATMOSPHERE
B
HANDLING EMISSIONS TO ATMOSPHERE
11
12
13
14
15
ISOMERIZER
DISTILLATION
DISTILLATION
K
SPENT CATALYST
CYCLOHEXANE PRODUCT WORKING STORAGE
CYCLOHEXANE PRODUCT TANK FARM STORAGE
BARGE - SHIP LOADING
PETROLEUM BYPRODUCT
(LESS VOLATILE THAN CYCLOHEXANE)
TO PETROCHEMICAL COMPLEX
A PROCESS EMISSION (FROM INDIVIDUAL EQUIPMENT VENTS DURING SHUTDOWN ONLY)
B STORAGE EMISSIONS
C HANDLING EMISSIONS
J FUGITIVE EMISSIONS - OVERALL PLANT
K SECONDARY EMISSION POTENTIAL
PETROLEUM SEPARATION PROCESS
CYCLOHEXANE
2 2
9104-10
JWB
3/9/78

There are no process emissions during normal operation. During emergency shutdowns individual equipment vents are opened as required.

Equipment leaks can be sources of benzene, cyclohexane, methane, or other petroleum compounds emissions. Leaks from heat exchangers into cooling water or steam production can be a potential fugitive loss. Fugitive losses are of special significance because of the high diffusivity of hydrogen at elevated temperatures and pressures and the extremely flammable nature of the liquid and gas processing streams.

Storage and handling emission sources (B and C, Fig. III-2) include cyclohexane storage and shipping. Storage of the petroleum feed stream is not included.

A potential source of secondary emissions (K, Fig. III-2) is catalyst handling. Caution is taken to remove the organic from the spent catalyst before it is replaced. The spent catalyst is sold for metal recovery.

D. REFERENCES*

1. K. Pardue, Cosden Oil and Chemical Co., Big Spring, TX, letter dated January 1978 to D. R. Goodwin, EPA, in response to EPA request for information on the cyclohexane process (on file at EPA, ESED, Research Triangle Park, NC.)

2. J. W. Blackburn, Trip Report on Site Visit to Exxon Chemical Company, Baytown, TX, Sept. 15, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. J. W. Blackburn, Trip Report on Visit to Phillips Puerto Rico Core, Inc., Guayama, PR, Sept. 20, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

4. F. A. Lowenheim and M. K. Moran, pp 298—303 in Faith, Keyes, and Clark's Industrial Chemicals, 4th ed., Wiley-Interscience, New York, 1975.

5. Telephone conversation on Jan. 6, 1978, between J. W. Blackburn and M. F. Potts, Process Engineering, Phillips Petroleum Company, Bartlesville, OK, relative to nonconfidential aspects of the petroleum separation process for cyclohexane manufacture.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. BENZENE HYDROGENATION PROCESS

The size of a cyclohexane plant is largely determined by the quantities of benzene and hydrogen available at a petrochemical complex. Each complex produces different petrochemicals and may use different primary petroleum feeds. The availability of benzene and hydrogen will also differ from site to site. Therefore it is not possible to specify the size of a typical plant that is expected to be constructed in the future.

1. Model Plants I, II, and III*

Since the capacities of actual cyclohexane plants vary widely (Table IV-1), three model plants with different capacities must be used. The three model plants for which emissions are described have capacities of 50, 150, and 250 Gg/hr, respectively, based on 8760 hr of operation per year.** The benzene hydrogenation process used in these plants is shown in Fig. III-1 and described in Sect. III. Platinum catalyst technology is used in all three plants. Air-dispersion parameters for each of the plants are given in Appendix B.

Benzene storage is sized to provide a 12-day supply. Working cyclohexane storage is 4 days, and tank-farm cyclohexane storage is 30 days. These storage

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*See p 1-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly production rate remians constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost effectiveness calculations the error introduced by assuming continuous operation is negligible.

Table IV-1. Cyclohexane Capacity Range by Producing Sites[a]

Capacity Range (Gg/yr)	Sites	Combined Capacity (Gg/yr)	Percent of Total Capacity
30—100	4	276	23.2
100—200	5	642	54.3
over 200	1	265	22.4
	10	1183	100.0

[a] For benzene hydrogenation process only.

capacities are consistent with data received from cyclohexane manufacturers.[1,2] Actual tank capacities are standard for typical API Standard 650 cone-roof tanks. The number of valves, pumps, and compressors used in the model plants is discussed in Sect. 2.b. The number of fugitive emission sources is based on data received from cyclohexane manufacturers[1,2] and is expected to be typical of the three model plants.

2. Sources and Emissions

a. Process Emissions (Shutdown)——There are no continuous process emissions from any of the cyclohexane model plants. Gaseous streams separated from the process that contain hydrogen and hydrocarbons (streams 8, 10, and 13, Fig. III-1) are sent to the fuel gas system at the petrochemical complex. This gas is used as fuel in process heaters supplying energy for other petrochemical processes.[1—6] Liquid hydrocarbons separated from recycled hydrogen (stream 12, Fig. III-1) are by-products that are used elsewhere at the petrochemical complex. No gas or liquid streams are discharged to the atmosphere on a continuous basis.

Some process emissions arise from shutdown of the process equipment. When equipment is shut down for maintenance, the high-pressure vapor is released to the fuel-gas system until the pressure in the equipment is the same as the pressure in the fuel-gas system. From this point on, the remaining pressure is relieved by discharging the vapor to a flare or to the atmosphere through a blowdown tank. The blowdown tank collects any liquid that may form during the depressurization process. During an emergency shutdown individual equipment vents are opened as required to relieve the pressure.

Table IV-2[7] lists the estimated depressurization-related emissions resulting from equipment shutdown and the assumptions on which the estimates are based. Two cases are presented. For Case I the emission is mostly hydrogen (equilibrium temperature is 25°C). For Case II the emission is totally cyclohexane vapor (equilibrium temperature is 81°C). Sample calculations relating to Table IV-2 are presented in Appendix C. Benzene is not present in depressurization-related emissions.[4]

b. Fugitive Emissions——Process pumps, valves, and compressors are potential sources of fugitive emissions. Each model plant is estimated to have 15 pumps

Table IV-2. Emissions Related to Depressurization of Process Equipment[a,b]

	Model Plant I	Model Plant II	Model Plant III
Capacity (Gg/yr)	50	150	250
Equipment internal void column (m^3)	11	33	55
Emissions (kg of VOC/yr)			
Case I			
Equilibrium temperature, 25°C; vapor composition, 12.8 mole % cyclohexane	25	74	123
Case II			
Equilibrium temperature, 81°C; vapor composition, 100 mole % cyclohexane	162	485	808

[a] See ref 7.

[b] Assumptions: 1. Initial pressure before depressurization, 517 kPa; final pressure after depressurization, 101 kPa. 2. Gases are ideal at these pressures and temperatures. 3. Cyclohexane is the only organic present. 4. No condensate collection devices (blowdown) are used. 5. Equipment void volume is proportional to capacity. 6. One complete depressurization each year.

handling light liquids (2 on benzene), 150 process valves on gas or vapor (15 on benzene), 150 process valves on light liquids (15 on benzene), 7 relief valves on gas or vapor (1 on benzene), 8 relief valves on light liquids (1 on benzene), and 1 hydrogen compressor. All pumps utilize mechanical seals. The factors used to establish the emission rates are shown in Appendix D.

c. Storage and Handling Emissions——Storage and handling emissions result from the handling of benzene and cyclohexane. For the model plants the sources are shown as B and C on the flow diagram, Fig. III-1. The storage tank specifications and conditions for all model plants are given in Table IV-3. The emissions listed in Tables IV-4, IV-5, and IV-6 are based on fixed-roof tanks, one-half full, and a 12.1°C diurnal temperature variation; the emission equations from AP-42[8] were used. Weather conditions correspond to data from the Houston, TX, area. Emissions calculated for fixed-roof tanks include working and breathing losses. Equations from AP-42 were used for these calculations also; however, breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing loss equation overestimates emissions.[9]

Handling emissions from loading cyclohexane in ships and barges were calculated with the equations in AP-42.[8] Sample calculations are presented in Appendix E.

d. Secondary Emissions——Secondary emissions resulting from catalyst replacement are small because of precautions taken to clean the organic from the catalyst before it is removed. Catalyst reclamation is performed off-site.[1,2]

The only process wastewater generated in cyclohexane manufacture is the effluent from absorbers in which aqueous streams are used to purify spent hydrogen.[3,4,6] These streams are sent to API separators. One plant reports 0.16-kg/hr VOC emitted by this secondary source.[3]

B. PETROLEUM SEPARATION PROCESS

The petroleum separation process shown in Fig. III-2 is expected to have emissions similar to those from the benzene hydrogenation process.[10] The major difference is the use of seven major processing steps instead of the three used in the benzene hydrogenation method. As in benzene hydrogenation, organic streams separated in the processing equipment are routed to other units in the petrochemical complex as by-products or are burned in process heaters as fuel gas.

Table IV-3. Model-Plant Storage Data

Content	Number of Tanks	Volume (m^3)[a]	Turnovers per year	Bulk Liquid Temperature (°C)
		Model Plant I, 50-Gg/yr Capacity		
Benzene	1	1,928	29.5	20.3
Cyclohexane	1	799	80.4	20.3
Cyclohexane	1	4,784	13.4	20.3
		Model Plant II, 150-Gg/yr Capacity		
Benzene	1	5,693	30.0	20.3
Cyclohexane	3	799	80.4	20.3
Cyclohexane	3	4,784	13.4	20.3
		Model Plant III, 250-Gg/yr Capacity		
Benzene	1	10,675	26.7	20.3
Cyclohexane	3	1,196	89.5	20.3
Cyclohexane	3	7,971	13.4	20.3

[a] Per tank.

Table IV-4. Benzene and Total VOC Uncontrolled Emissions for Model Plant I

Source	Stream Designation[a]	Emission Ratio[b]		Emission Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC
Process emissions, shutdown	A		3.2		0.02
Storage	B	425	1308	2.42	7.47
Handling	C		147		0.84
Fugitive[c]	J	154	1419	0.88	8.1
Secondary	K		13		0.07[d]
Total				3.30	16.50

[a] See Fig. III-1.

[b] g of emission per Mg of cyclohexane produced; emission ratios are valid only for the model plant operating at capacity.

[c] See Appendix D.

[d] Only for plants employing aqueous absorption for hydrogen purification.

Table IV-5. Benzene and Total VOC Uncontrolled Emissions for Model Plant II

Source	Stream Designation[a]	Emission Ratio[b]		Emission Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC
Process emissions, shutdown	A		3.2		0.05
Storage	B	421	1305	7.21	22.3
Handling	C		148		2.53
Fugitive[c]	J	51.4	473	0.88	8.1
Secondary	K		13		0.22[d]
Total				8.09	33.20

[a] See Fig. III-1.

[b] g of emission per Mg of cyclohexane produced; emission ratios are valid only for the model plant operating at capacity.

[c] See Appendix D.

[d] Only for plants employing aqueous absorption for hydrogen purification.

Table IV-6. Benzene and Total VOC Uncontrolled Emissions for Model Plant III

Source	Stream Designation[a]	Emission Ratio[b]		Emission Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC
Process emissions, shutdown	A		3.2		0.09
Storage	B	420	1256	12.0	35.9
Handling	C		148		4.22
Fugitive[c]	J	30.8	284	0.88	8.1
Secondary	K		13		0.37[d]
Total				12.88	48.68

[a] See Fig. III-1.

[b] g of emission per Mg of cyclohexane produced; emission ratios are valid only for the model plant operating at capacity.

[c] See Appendix D.

[d] Only for plants employing aqueous absorption for hydrogen purification.

1. Model Plant

The model plant producing cyclohexane by petroleum separation has a capacity of 100 Gg/yr of cyclohexane based on 8760 hr of operation per year. Storage requirements for the working cyclohexane tanks are 4 days of retention time; tank-farm cyclohexane storage is 30 days of retention time.[1,2] (Storage for this process may sometimes be combined with storage for other processes in those locations where cyclohexane is manufactured by both processes.) No storage is assumed for the petroleum feed.

The number of valves, pumps, and compressors is discussed in Sect.B.2.b. These sources were estimated from data supplied on the benzene hydrogenation process.[1,2]

2. Sources and Emissions

a. Process Emissions (Shutdown)——The emissions from this source are estimated from the values given in Table IV-2, with allowance made for an increased internal void volume for the equipment related to this process. An internal void volume of 77 m^3 results in emissions of 177 kg of VOC per depressurization for Case I and in 1132 kg of VOC per depressurization for Case II, as defined in the table. Assumptions for these calculations are also given in Table IV-2. One complete equipment depressurization per year is assumed and the worst case, Case II, is used.

b. Fugitive Emissions——Process pumps, valves, and compressors are potential sources of fugitive emissions. Each model plant is estimated to have 35 pumps handling light liquids, 200 process valves on gas or vapor, 500 process valves on light liquids, 10 relief valves on gas or vapor, 25 relief valves on light liquids, and 1 hydrogen compressor. All pumps utilize mechanical seals. The factors used to establish the emission rates are shown in Appendix D.

c. Storage and Handling Emissions——Storage and handling emissions result from the handling of petroleum liquids and cyclohexane. The sources for the model plant for this process are shown as B and C on the flow diagram, Fig. III-2. The storage tank specifications and conditions are given in Table IV-7. The emissions given in Table IV-8 are based on fixed-roof tanks, one-half full, and a 12.1°C diurnal temperature variation; emission equations from AP-42[8] were used, together with the breathing loss equation adjustment discussed in Sect. A.2.c.

Table IV-7. Storage Data for Model Plant Using Petroleum Separation Process

Content	Number of Tanks	Volume (m^3)[a]	Turnovers per year	Bulk Liquid Temperature (°C)
Petroleum liquid	None			
Cyclohexane	2	799	80.4	20.3
Cyclohexane	3	3843	11.1	20.3

[a] Per tank.

Table IV-8. Total VOC Uncontrolled Emissions from Plant Using Petroleum Separation Process

Source	Stream Designation[a]	Emission Ratio[b]	Emission Rate (kg/hr)
Process emissions, shutdown	A	11	0.13
Storage	B	873	9.97
Handling	C	148	1.69
Fugitive[c]	J	1367	15.6
Secondary	K		
Total			27.39

[a] See Fig. III-2.

[b] g.of emission per Mg of cyclohexane produced; emission ratios are valid only for the model plant operating at capacity.

[c] See Appendix D.

Handling emissions from loading cyclohexane in ships and barges were calculated with the equations from AP-42.[8]

d. Secondary Emissions—Secondary emissions result only from catalyst handling and are small because of precautions taken by the manufacturers before removal of the catalyst. Catalyst reclamation is performed off-site.[1,2]

No process wastewater is expected. Aqueous streams are not used to purify hydrogen.

C. REFERENCES*

1. J. W. Blackburn, Trip Report on Visit to Exxon Chemical Company, Baytown, TX, Sept. 15, 1977 (on file at the EPA, ESED, Research Triangle Park, NC).
2. J. W. Blackburn, Trip Report on Visit to Phillips Puerto Rico Core, Inc., Guayama, PR, Sept. 20, 1977 (on file at the EPA, ESED, Research Triangle Park, NC).
3. M. P. Zanotti, Gulf Oil Col, USA, Port Arthur, TX, letter dated Jan. 26, 1978, to D. R. Goodwin, EPA, in response to EPA request for information on the cyclohexane process (on file at EPA, ESED, Research Triangle Park, NC).
4. K. Pardue, letter dated Jan. 24, 1978, to D. R. Goodwin, EPA, Cosden Oil and Chemical Co., Big Spring, TX, in response to EPA request for information on the cyclohexane process (on file at EPA, ESED, Research Triangle Park, NC).
5. R. L. Chaffin, Champlin Petroleum Co., Corpus Christi, TX, letter dated Jan. 25, 1978, to D. R. Goodwin, EPA (on file at EPA, ESED, Research Triangle Park, NC).
6. W. W. Dickinson, Sun Petroleum Production Co., Tulsa, OK, letter dated Jan. 26 1978, to D. R. Goodwin, EPA (on file at EPA, ESED, Research Triangle Park, NC).
7. R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, The Properties of Gases and Liquids, 3d ed., McGraw-Hill, New York, 1977.
8. C. C. Masser, "Storage of Petroleum Liquids," pp 4.31 to 4.3-17 in Compilation of Air Pollutant Emission Factors, AP-42, Part A, 3d ed. (August 1977).
9. Letter dated May 30, 1979, from E. C. Pulaski, TRW, Inc. to Richard Burn, EPA.
10. J. W. Blackburn, IT Enviroscience, Inc., telephone conversation on Jan. 6, 1978, with M. F. Potts, Phillips Petroleum Co., Bartlesville, OK.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. BENZENE HYDROGENATION PROCESS

1. Process Sources

The gas vented to the atmosphere when equipment is depressurized during shutdown can be routed to a flare. A flare could be dedicated for this emission or another available flare may be used. Flare efficiencies are dependent on design, gas flow, and size. When in smokeless operation and operating with a gas flow of 10% to 100% of the maximum smokeless design, the efficiencies should be greater than 98% for flares with tips greater than 12 in. and greater than 99% for flares with tips less than 12 in. An efficiency factor of 98% will be assumed in this study since the flare utilized may have been designed for a variety of applications. The cost effectiveness of flares is not presented in Sect. VI because the flare would probably not be dedicated solely to cyclohexane process duty.

2. Fugitive Sources

Controls for fugitive sources will be discussed in a future document covering fugitive emissions from the synthetic organic chemicals manufacturing industry. Controlled fugitive emissions have been calculated based on the factors given in Appendix D and are included in Tables V-1, 2, and 3.

3. Storage and Handling Sources

Storage guidelines for all organic compounds will be covered in a future EPA document. Control for storage losses involves the use of floating-roof tanks* or retrofitting floating roofs to existing fixed-roof tanks. Emissions listed in Tables V-1 through V-3 assume a contact-type internal floating roof with secondary seals is used and will reduce fixed-roof-tank emissions by 85%.[3] Control of cyclohexane loading emissions is not practiced in the cyclohexane industry. No reduction in loading emissions is assumed for this study. Control systems using vapor-recovery, dedicated flares, and other technologies have been used in the chemical industry to control organic emissions resulting from chemical loading.

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*Consist of internal flaoting covers or covered floating roofs as defined in API-2519, 2d ed., 1976 (fixed-roof tanks with internal floating device to reduce vapor loss).

Table V-I. Controlled Benzene and Total VOC Emissions for Model Plant I (Internal-Floating-Roof Tanks)

Source	Stream Designation[a]	Emission Ratio[b]		Emission Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC
Process emissions, shutdown	A		0.06		0.0003
Storage	B	63.6	196	0.36	1.12
Handling	C		147		0.84
Fugitive[c]	J	35.0	314	0.20	1.79
Secondary	K		13		0.07
Total				0.56	3.82

[a] See Fig. III-1.

[b] g of emission per Mg of cyclohexane produced; emission ratios are valid only for the model plant operating at capacity.

[c] See Appendix B.

[d] Only for plants employing aqueous absorption for hydrogen purification.

Table V-2. Controlled Benzene and Total VOC Emissions for Model Plant II (Internal-Floating-Roof Tanks)

Source	Stream Designation[a]	Emission Ratio[b]		Emission Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC
Process emissions, shutdown	A		0.06		0.001
Storage	B	63.2	196	1.08	3.35
Handling	C		148		2.53
Fugitive[c]	J	11.7	105	0.20	1.79
Secondary	K		13		0.22[d]
Total				1.28	7.89

[a] See Fig. III-1.

[b] g of emission per Mg of cyclohexane produced; emission ratios are valid only for the model plant operating at capacity.

[c] See Appendix D.

[d] Only for plants employing aqueous absorption for hydrogen purification.

Table V-3. Controlled Benzene and Total VOC Emissions for Model Plant III (Internal-Floating-Roof Tanks)

		Emission Ratio (g/Mg)[b]		Emission Rate (kg/hr)	
Source	Stream Designation[a]	Benzene	Total VOC	Benzene	Total VOC
Process emissions, shutdown	A		0.06		0.002
Storage	B	63.0	188	1.80	5.38
Handling	C		148		4.22
Fugitive[c]	J	7.0	62.7	0.20	1.79
Secondary	K		13		0.37[d]
Total				2.00	11.76

[a] See Fig. III-1.

[b] g of emission per Mg of cyclohexane produced; emission ratios are valid only for the model plant operating at capacity.

[c] See Appendix D.

[d] Only for plants employing aqueous absorption for hydrogen purification.

4. Secondary Sources

Secondary emissions are small. Plants using aqueous absorption to purify the hydrogen employ API separators to prevent water pollution. Emissions listed in Tables V-1 through V-3 are based on data from industry.[4]

B. PETROLEUM SEPARATION PROCESS

Control devices listed for the benzene hydrogenation process are also applicable to the petroleum separation process. Table V-4 gives the controlled emissions from the petroleum separation process, with internal-floating-roof tanks the major control device.

Table V-4. Model-Plant Controlled Total VOC Emissions for Petroleum Separation Process (Internal-Floating-Roof Tanks)

Source	Designation[a]	Emission Ratio (g/Mg)[b]	Emission Rate (kg/hr)
Process emissions, shutdown	A	0.22	0.003
Storage	B	135	1.55
Handling	C	148	1.69
Fugitive[c]	J	335	3.82
Secondary	K		
Total			7.06

[a] See Fig. III-2.

[b] g of emission per Mg of cyclohexane produced; emission ratios are valid only for the model plant operating at capacity.

[c] See Appendix D.

C. REFERENCES*

1. V. Kalcevic, IT Enviroscience, Inc., Flares and the Use of Emissions as Fuels (in preparation for EPA, ESED, Research Triangle Park, NC).

2. C. C. Masser, "Storage of Petroleum Liquids," pp 4.3-1 to 4.3-17 in Compilation of Air Pollutant Emission Factors, AP-42, Part A, 3d ed. (August 1977).

3. Letter dated Aug. 15, 1979, from W. T. Moody, TRW, Inc. to Dave Beck, EPA.

4. Nonconfidential information received January 1978 from Gulf Oil Company—USA, Port Arthur Refinery, TX (on file at ESED, EPA, Research Triangle Park, NC).

*Usually, when a reference number is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved.

VI. SUMMARY

Two site visits and additional contact with the industry indicated that emissions expressed in the literature are nearly 10 times as high as emissions found in this study, which possibly reflects a greater concern for reuse of spent hydrogen and petroleum by-products in today's market. This increased concern has grown from a change in the economics of the petrochemical industry during the last decade. Cyclohexane manufacture is currently one of the lowest emitters of the eight benzene-consuming processes studied by IT Enviroscience.

Cyclohexane is predominantly used in the production of caprolactam, adipic acid, and hexamethylenediamine intermediates in the manufacture of nylon 6 and nylon 6,6. The demand for cyclohexane is expected to grow at a rate of 5% per year through 1982. The present capacity of the nine United States cyclohexane producers should be adequate throughout this period.

The predominant cyclohexane manufacturing process is the catalytic hydrogenation of benzene, which is capable of producing 99.9% pure cyclohexane. The process generates significant quantities of energy, usually as steam, and also as fuel gas. Organic-laden spent hydrogen is recovered by hydrogen purification processes and is reused in cyclohexane and other hydrogen-consuming processes.

Because of the scarcity of hydrogen in today's petrochemical refinery, every effort is made to prevent hydrogen losses as emissions. This also results in very low organic emissions. Potential emissions are eliminated by recycling the process streams as by-products or by using them as fuel.

In a cyclohexane plant organic emissions can occur from benzene and cyclohexane storage and cyclohexane loading operations. If fugitive sources are not controlled, fugitive losses can be a significant organic source. Table VI-1 summarizes the uncontrolled and controlled emissions from the model plants using the benzene hydrogenation process; Table VI-2 summarizes the model-plant's uncontrolled and controlled emissions for the petroleum separation process.

The combined VOC emissions from all domestic cyclohexane production would be 336 kg/hr if uncontrolled and 78 kg/hr if controlled.

Table VI-1. Summary of Emissions for Benzene Hydrogenation Model Plants[a] (Internal-Floating-Roof Storage Emission Control)

	Emissions (kg/hr) for Model Plant I				Emissions (kg/hr) for Model Plant II				Emissions (kg/hr) for Model Plant III			
	Uncontrolled		Controlled		Uncontrolled		Controlled		Uncontrolled		Controlled	
Emission Source	Benzene	VOC	Benzene	VOC	Benzene	VOC	Benzene	VOC	Benzene	VOC	Benzene	VOC
Process		0.02		0.0003		0.05		0.001		0.09		0.002
Storage	2.42	7.47	0.36	1.12	7.21	22.3	1.08	3.35	12.0	35.9	1.80	5.38
Handling		0.84		0.84		2.53		2.53		4.22		4.22
Fugitive	0.88	8.1	0.20	1.79	0.88	8.1	0.20	1.79	0.88	8.1	0.20	1.79
Secondary		0.07[b]		0.07[b]		0.22[b]		0.22[b]		0.37[b]		0.37[b]
Total	3.30	16.50	0.56	3.82	8.09	33.20	1.28	7.89	12.88	48.68	2.00	11.76

[a] Capacities: Model Plant I, 50 Gg/yr; Model Plant II, 150 Gg/yr; Model Plant III, 250 Gg/yr.

[b] Only for plants employing aqueous absorption for hydrogen purification.

Table VI-2. Summary of VOC Emissions for Petroleum Separation Process (Internal-Floating-Roof Tank Emission Control)

Emission Source	Uncontrolled (kg/hr)	Controlled (kg/hr)
Process	0.13	0.003
Storage	9.97	1.55
Handling	1.69	1.69
Fugitive[a]	15.6	3.82
Secondary		
Total	27.39	7.06

[a] See Appendix D.

The manufacturers presently use a mixture of fixed-roof and floating-roof storage tanks for organic storage. Use of floating-roof tanks is a significant control measure. The actual national emissions therefore would range between the uncontrolled and controlled values stated above. An assumption of 50% floating-roof usage would indicate the current national VOC emissions from cyclohexane to be about 200 kg/hr. Exact calculation of national emissions is not possible since the actual storage facilities for each manufacturer are not presently known. Information regarding the emission control measures presently practiced in the cyclohexane industry is given in Appendix F.

APPENDIX A

Table A-1. Physical Properties of Benzene, Cyclohexane, and Hygrogen

	Benzene[a]	Cyclohexane[b]	Hydrogen[b]
Synonyms	Benzol, coal naphtha, phenylhydride	Hexahydrobenzene, hexanaphthene, hexamethylene	
Molecular fomula	C_6H_6	C_6H_{12}	H_2
Molecular weight	78.11	84.16	2.01
Physical state	Liquid	Liquid	Gas
Vapor pressure	95.9 mm Hg at 25°C	98.14 mm Hg at 25°C (96.97 mm Hg at 25°C)[c]	
Vapor specific gravity	2.77	2.90	
Boiling point	80.1°C at 760 mm Hg	80.7°C at 760 mm Hg	
Melting point	5.5°C	6.3°C	
Liquid specific gravity	0.8787 at 20°C/4°C	0.77855 at 20°C/4°C	
Water solubility	1.79 g/liter	<1 g/liter	
Octanol/water partition coefficient	2.28		

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[a] From J. Dorigan, B. Fuller, and R. Duffy, "Benzene," p AI-102 in Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-c), MTR-7248, Rev 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

[b] From J. Dorigan, B. Fuller, and R. Duffy, "Cyclohexane," ibid, p AI-318.

[c] From R. C. Reid et al., The Properties of Gases and Liquids, McGraw-Hill, New York, 1977.

APPENDIX B

Table B-1. Air-Dispersion Parameters

Emission Source	Number of Sources	Emission Rate (g/sec)	Tank Height (m)	Tank Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)
Model Plant I, 50 Gg/yr						
Storage						
Uncontrolled						
Benzene	1	0.67	14.63	12.95	Ambient	
Cyclohexane	1	0.45	9.75	10.21	Ambient	
Cyclohexane	1	0.95	12.19	22.35	Ambient	
Storage						
Controlled[a]						
Benzene	1	0.10	14.63	12.95	Ambient	
Cyclohexane	1	0.068	9.75	10.21	Ambient	
Cyclohexane	1	0.14	12.19	22.35	Ambient	
Fugitive						
Uncontrolled		2.25			Ambient to 530	
Controlled		0.50			Ambient to 530	
Handling		0.23			Ambient	
Model Plant II, 150 Gg/yr						
Storage						
Uncontrolled						
Benzene	1	2.00	12.19	24.38	Ambient	
Cyclohexane	3	0.45	9.75	10.21	Ambient	
Cyclohexane	3	0.95	12.19	22.35	Ambient	
Controlled						
Benzene	1	0.30	12.19	24.38	Ambient	
Cyclohexane	3	0.068	9.75	10.21	Ambient	
Cyclohexane	3	0.14	12.19	22.35	Ambient	

Table B-1. (Continued)

Emission Source	Number of Sources	Emission Rate (g/sec)	Tank Height (m)	Tank Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)
Fugitive						
Uncontrolled		2.25			Ambient to 530	
Controlled		0.50			Ambient to 530	
Handling		0.23			Ambient	
Model Plant III, 250 Gg/yr						
Storage						
Uncontrolled						
Benzene	1	3.33	14.63	30.48	Ambient	
Cyclohexane	3	0.68	12.19	11.18	Ambient	
Cyclohexane	3	1.52	17.07	24.38	Ambient	
Controlled						
Benzene	1	0.50	14.63	30.48	Ambient	
Cyclohexane	3	0.10	12.19	11.18	Ambient	
Cyclohexane	3	0.23	17.07	24.38	Ambient	
Fugitive						
Uncontrolled		2.25			Ambient to 530	
Controlled		0.50			Ambient to 530	
Handling		0.23			Ambient	
Model Plant, Petroleum Separation Process						
Storage						
Uncontrolled						
Cyclohexane	2	0.66	9.75	10.21	Ambient	
Cyclohexane	3	0.45	14.63	18.29	Ambient	

Table B-1. (Continued)

Emission Source	Number of Sources	Emission Rate (g/sec)	Tank Height (m)	Tank Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)
Controlled						
Cyclohexane	2	0.098	9.75	10.21	Ambient	
Cyclohexane	3	0.067	14.63	18.29	Ambient	
Fugitive						
Uncontrolled		4.33			Ambient to 530	
Controlled		1.06			Ambient to 530	
Handling		0.47			Ambient	

APPENDIX C

SAMPLE CALCULATIONS FOR PROCESS DEPRESSURIZATION LOSSES

CALCULATION FOR PROCESS LOSSES DUE TO SHUTDOWN DEPRESSURIZATION

Case I: Equilibrium flash temperature: 25°C

Initial pressure 75 psia
3875 mm Hg
0.517 MPa

Final pressure 14.7 psia
760 mm Hg
0.101 MPa

Composition of escaping gas at equilibrium:

$$Y\ (\text{mole fraction}) = \frac{\text{vapor pressure of cyclohexane at }25^\circ\text{C}}{\text{total final pressure}}.$$

$$\text{vapor pressure of cyclohexane} = e^{\left(15.7527 - \frac{2766.63}{T\ (K) - 50.50}\right)^{*}}$$

vapor pressure of cyclohexane at 25°C = 96.97 mm Hg.

$$y\ (\text{mole fraction}) = \frac{96.97}{760} = 0.128.$$

Moles of escaping gas at equilibrium

$$\frac{359\ \text{scf}}{\text{lb mole}} \times \frac{298\ \text{K}}{273\ \text{K}} \times \frac{760\ \text{mm Hg}}{3878\ \text{mm Hg}} = 76.8\ \text{ft}^3/\text{lb-mole (at equilibrium conditions)}.$$

$$\frac{1160\ \text{ft}^3\ \text{(equipment volume)}}{76.8\ \text{ft}^3/\text{lb-mole}} = 15.1\ \text{lb-mole released.}$$

Cyclohexane released

15.1 (lb-mole of gas released) X 0.128 (mole fraction of cyclohexane)

= 1.933 lb-moles of cyclohexane,
= 163 lb of cyclohexane,
= 74 kg of cyclohexane.

Case II: Pure cyclohexane vapor released (temperature = 81°C)

Initial pressure 75 psia
3875 mm Hg
0.517 MPa

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[*] Reid et al., The Properties of Gases and Liquids, McGraw-Hill, New York, 1977.

Final pressure	14.7 psia
	760 mm Hg
	0.101 MPa

Composition of escaping gas

$$y \text{ (mole fraction)} = \frac{\text{vapor pressure at } 81^\circ\text{C}}{760 \text{ mm Hg}} .$$

y (mole fraction) - 1.0.

Moles of escaping gas at equilibrium

$$\frac{359 \text{ scf}}{\text{lb-mole}} \times \frac{354 \text{ K}}{273 \text{ K}} \times \frac{760 \text{ mm Hg}}{3878 \text{ mm Hg}} = 91.23 \text{ ft}^3\text{/lb-mole}$$

$$\frac{1160 \text{ ft}^3}{91.23 \text{ ft}^3\text{/lb-mole}} = 12.72 \text{ lb-mole of escaping gas}$$

Amount of cyclohexane relased

$$12.72 \text{ lb-moles of gas} \times \frac{\text{lb-mole of cyclohexane}}{\text{lb-mole of gas}} \times 84 = 1068 \text{ lb of cyclohexane},$$

$$= 485 \text{ kg of cyclohexane.}$$

APPENDIX D

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX E

SAMPLE CALCULATIONS FOR HANDLING LOSSES

1. Data

1976 capacity shipped = 342,105 bbls X 3 = 1,026,315 bbls/yr.

By tanker = 90% X 1,026,315 = 924,000 bbls
tanker capacity = 300,000 bbls 3 tankers/yr.

By barge = 1,026,315 - 900,000 = 126,315 bbls
barge capacity = 13,000 bbls 10 barges/yr.

2. Product Data

Chemical, cyclohexane

Molecular weight = 84.16.

Specific gravity = 0.779 (20/4), 0.7834 (60°F/60°F).

Vapor pressure = 60 mm Hg at 14.7°C,
100 mm Hg at 25.5°C.

40°F	50°F	60°F	70°F	80°F	90°F	100°F
0.677 psia	0.928 psia	1.218 psia	1.605 psia	2.069 psia	2.610 psia	3.249 psia

Ambient average temperature = 79.3°F.

3. Loading Loss, Equations, and Terms

$L = 12.46 \frac{SPM}{T}$ lb/10^3 gal of liquid loaded.

S = 0.2 for ships; 0.5 for barges.

P = true vapor pressure: assume 2.069 psia at 80°F.

M = Molecular weight = 84.16 lb/lb-mole.

T = bulk temperature: assume 79°F + 460° = 539°R.

3.1. For 3 tankers/yr:

$$L \text{ (tankers)} = \frac{(12.46)\ (0.2)\ (2.069)\ (84.16)}{539} = 0.80 \text{ lb/1000 gal.}$$

$$\frac{0.80 \text{ lb}}{1000 \text{ gal}} \times 300{,}000 \text{ bbl} \times \frac{42 \text{ gal} \times 3 \times \text{ton}}{\text{bbl} \times 2000 \text{ lb}} = 15.20 \text{ tons per year.}$$

3.2. For 10 barges/yr:

$$L \text{ (barge)} = \frac{(12.46)\ (0.5)\ (2.069)\ (84.16)}{539}$$

$$= \frac{2.01 \text{ lb}}{1000 \text{ gal}} \times 13{,}000 \text{ bbl} \times \frac{42 \text{ gal} \times 10 \times \text{tons}}{\text{bbl} \times \text{yr} \times 2000 \text{ lb}} = 5.49 \text{ tons per year.}$$

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*Supplement No. 7 for Compilation of Air Pollutant Emission Factors, API Bulletin 42, 2d ed., pp 4.3-6 to 4.3311, American Petroleum Institute, Washington, DC (April 1977).

4. Total Emissions (Loading)

Tankers = 15.20 tons/yr

Barges = 5.49 tons/yr

20.69 tons/yr

APPENDIX F

EXISTING PLANT CONDITIONS

Table F-1 lists the control devices reported to be in use by industry.[1—6] Further information on the processes follows:

A. EXXON AT BAYTOWN, TX[2]

1. Process Description

The nameplate capacity of Exxon's cyclohexane production plant is 3000 bbl/day of 99.95 mole % cyclohexane. The plant was started in 1958, with a process expansion in 1967.

The process was licensed from UOP. The hydrogen and recycled cyclohexane flow in series through the reactors and benzene is added in parallel to each of the reactors. The process uses a platinum metal catalyst, which has a life of about 10 years.

Variations between the Exxon process and a standard process are a "methanator" reactor, which catalytically converts trace quantities of CO in the feed hydrogen to CO_2; five cyclohexane reactors; a scrubber that removes cyclohexane vapor from the spent-hydrogen stream and uses benzene as the scrubbing fluid; a second scrubber that removes benzene from the spent-hydrogen stream and uses toluene as the scrubbing fluid; and the ability to vary the sources and sinks of feed hydrogen and spent hydrogen as the overall plant-wide hydrogen demands vary.

The necessity to vary the hydrogen feed stream and spent-hydrogen stream is important. The Exxon chemical plant is located in close proximity to an Exxon petroleum refinery. These two plants are separated adminstratively, but they transfer chemical raw materials and products from one to the other on a continuous basis. All the benzene feed to the cylcohexane unit is produced by extraction and purification of a refinery side stream containing high concentrations of aromatics. The hydrogen for the cyclohexane unit originates from reformers in the refinery. However, hydrogen purity for cyclohexane production, as well as for other hydrogen-consuming processes, must be higher than that obtained directly from the reformers. Therefore during the past decade cryogenic

Table F-1. Control Devices Currently Used by the Cyclohexane Industry in the United States

Company	Floating-Roof Tanks (Open Top and Internal)		
	Benzene Storage	Cyclohexane Storage	Flares (Process or Fugitive)
Cosden Oil[a]	N.D.[b]	N.D.	Yes
Corco Cyclohexane	N.D.	N.D.	N.D.
Exxon Chemical[c]	Yes	Yes	No
Gulf Oil[d]	N.D.	N.D.	N.D.
Phillips Petroleum			
Borger, TX	N.D.	N.D.	N.D.
Sweeny, TX	N.D.	N.D.	N.D.
Guayama, PR[e]	No	Yes	Yes
Sun[f]	N.D.	N.D.	N.D.
Texaco	N.D.	N.D.	N.D.
Union Oil of California	N.D.	N.D.	N.D.
Champlin Petroleum[g]	N.D.	N.D.	Yes

[a] See ref 1.

[b] No data.

[c] See ref 2.

[d] See ref 3.

[e] See ref 4.

[f] See ref 5.

[g] See ref 6.

hydrogen purification units have been added to increase the hydrogen purity from 70 to 85 mole % to the 95 mole % required for cyclohexane and other processes.

In a petrochemical complex such as Exxon's the supply and demand of the valuable chemical, hydrogen, often helps to determine the overall product mix of the plant. Production of compounds requiring hydrogen is lowered when the hydrogen supply is short. The sources of feed hydrogen and the "consumers" of spent hydrogen at the Baytown plant are flexible so that cyclohexane operation can be continued during changes in the hydrogen supply situation. Every attempt is made to recycle hydrogen-rich gases to processes directly or by purification units. Gases containing hydrogen but rich in organics are candidates for the plant-wide fuel gas system. In this case heat is recovered from the gas. Direct loss of hydrogen resulting from continuous or intermittent atmospheric process emissions or from the lack of heat recovery is avoided. Therefore loss of organics in these process-related streams is minimized. Exxon estimates that about one-fifth of the spent hydrogen from cyclohexane production is routed to the adjacent refinery complex, with the bulk sent to a localized cryogenic purifier. The direct recycle of spent hydrogen into the hydrogen feed to the cyclohexane plant occurs when there is a shortage of hydrogen on a plant-wide basis.

The off-gas from the stabilizer still, which is sent to the plant-wide fuel gas system, is composed predominently of H_2 and CH_4 staturated with cyclohexane.

2. Startup/Shutdown

The cyclohexane unit does not require annual shutdowns for maintenance; but when the unit does have to be shut down, the procedure is to stop the benzene feed to the reactors. The hydrogen and cyclohexane recycled flow is continued until the reactor temperatures are at a safe level. During this period the spent hydrogen is sent to the fuel gas manifold, where it remains until the pressure in the system is the same as the manifold back-pressure. The remaining pressure (~75 psi) is vented to the atmosphere through a condensible blowdown drum. This drum catches some of the organic that would otherwise be emitted to the atmosphere. This emission has not been quantified.

In an emergency condition, which is estimated to occur about twice a year, only the piece of equipment affected is depressurized. Again, the pressure is relieved until it is the same as the fuel-gas manifold back-pressure. The remainder is vented to the atmosphere. No quantitative data involving this intermittent emission were obtained.

B. PHILLIPS AT GUAYAMA, PR[4]

1. Process Description

Most of the information regarding the process description is confidential and therefore is not included. However, the following information was given in a non-confidential manner:

The cyclohexane process at Guayama is a Phillips process and was developed within the corporation. It is similar to the hydrogenation production units at Phillips Petroleum, Borger, TX, and Sweeny, TX, locations. The original designs for the American plants were based on a similar benzene hydrogenation plant in Antwerp, Belgium.

The Guayama plant was built in 1967 and was started up in 1968. There have been two expansions, the most recent one occurring in 1976. The present capacity is 6000 bbl/day of 99.5 mole % cyclohexane.

The cyclohexane unit at Guayama is part of a petrochemical operation using petroleum naphtha as the fundamental feed. A desulfurization unit removes sulfur from the organic streams, allowing the use of a nickel catalyst to hydrogenate benzene to cyclohexane. Nickel catalysts are poisoned by sulfur compounds.

The catalyst life for this process is about 4 years. In other words, one of the four catalyst-containing reactors is replaced each year. Exothermic runaway reactions are possible due to the type of catalyst used, and therefore elaborate temperature monitoring procedures are used to predict the changes in catalyst performance and impending runaway reactions. The probability of a runaway or exothermic reaction increases as the catalyst ages. When it is suspected that a bed is involved, it is removed from the system and the catalyst is replaced.

When a bed is to be replaced, it is isolated from the system and allowed to cool. Before the catalyst is removed from the reactor, it is purged with nitrogen under a 5-psia vacuum supplied by two jets. The off-gas from this system is sent to a flare. The nitrogen is used to remove organics from the catalyst and to prevent a hydrogen explosion. The bed is then removed and sold for nickel recovery. New catalyst in reduced form is loaded into the reactor and is then oxidized with hot air and steam. A small process heater using fuel gas supplies the hot air and steam for the oxidizing process. It consumes less than 4 million Btu/hr when in operation and is used from 10 to 20 days a year. Complete combustion is assumed by Phillips.

Hydrogen is in short supply at Guayama, and the cyclohexane unit has a lower priority for hydrogen than other processes. For this reason production fluctuates with hydrogen availability. Spent hydrogen from the cyclohexane process is purified in a cryogenic system, also developed by Phillips. Purified hydrogen is routed back to the cyclohexane unit and elsewhere in the plant.

2. Startup/Shutdown

The public electrical power system in Guayama is unreliable, and plant personnel estimate that power failures occur about once a month. When a power failure occurs, the hydrogenation reaction may be exothermic. The benzene feed must be stopped, and the hydrogen flow must be maintained to sustain internal cooling and prevent a runaway reaction. The compressor supplying hydrogen to the reactors is driven by a steam turbine instead of an electric motor. The probability of power and steam being lost simultaneously is small and occurrences of reactor runaways are minimized. When a runaway reaction is not controlled by all these precautions, it is vented to a flare. No quantitative data are available on this emission, but it is felt to be very low.

C. GULF OIL AT PORT ARTHUR, TEXAS[3]

Gulf Oil lists the following description of the off-gas from a water absorber used to purify spent hydrogen:

Temperature: ambient

Flow: 0.76 lb/hr

Composition	Amount (wt %)
Nitrogen	2.5
Hydrogen	41.5
Methane	9.0
Ethane	16.2
Propane	18.1
Isobutane	1.3
n-Butane	8.0
Isopentane	1.7
n-Pentane	1.7
	100.0

D. SUN PETROLEUM AT TULSA, OK.[5]

Information from Sun Petroleum shows no emissions.

E. COSDEN OIL AND CHEMICAL COMPANY AT BIG SPRING, TX[1]

Information from Cosden gives flow and composition information for pressure-relief valves, fuel-gas streams, and off-gas from process heaters. Cosden also claims to have no measurable levels of benzene in their streams except for the reactor feed streams.

F. CHAMPLIN PETROLEUM AT CORPUS CHRISTI, TX.[6]

Little data were given by Champlin. Off-gases from column reboilers are sent to smokeless flares. Fuel-gas streams are recovered.

G. REFERENCES*

1. K. Pardue, Cosden Oil and Chemical Co., Big Spring, TX, letter dated January 1978 to D. R. Goodwin, EPA, in response to EPA request for information on cyclohexane prodess (on file at EPA, ESED, Research Triangle Park, NC).

2. J. W. Blackburn, IT Enviroscience, Inc., Trip Report on Visit to Exxon Chemical Company, Baytown, TX, Sept. 15, 1977 (on file at the EPA, ESED, Research Triangle Park, NC).

3. M. P. Zanotti, Gulf Oil Company—USA, Port Arthur TX, letter dated Jan. 26, 1978 to D. R. Goodwin, EPA, in response to EPA request for information on cyclohexane process (on file at EPA, ESED, Research Triangle Park, NC).

4. J. W. Blackburn, IT Enviroscience, Inc., Trip Report on Visit to Phillips Puerto Rico Core, Inc., Guayama, PR, Sept. 20, 1977 (on file at the EPA, ESED, Research Triangle Park, NC).

5. Sun Petroleum Production Co., Tulsa Refinery (on file at ESED, EPA, Research Triangle Park, NC).

6. W. W. Dickinson, Champlin Petroleum Co., Corpus Christi TX, letter dated Jan. 26, 1978 to D. R. Goodwin, EPA, in response to EPA request for information on cyclohexane process (on file at EPA, ESED, Research Triangle Park, NC).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 2

CYCLOHEXANOL/CYCLOHEXANONE

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II-. INDUSTRY DESCRIPTION

A. SELECTION OF CYCLOHEXANOL/CYCLOHEXANONE

Cyclohexanol and cyclohexanone are currently synthesized industrially in either of two basic processes -- cyclohexane oxidation or phenol hydrogenation. Generally, both cyclohexanol and cyclohexanone are formed simultaneously in either process. The ratio of cyclohexanol to cyclohexanone in the product depends on the catalyst used and the process operating conditions. Since manufacture of some products, primarily adipic acid, does not require separation of cyclohexanol/cyclohexanone product into its individual constitutuents, this product report addresses both compounds simultaneously.[1]

Cyclohexanol/cyclohexanone was selected as a product for study for the following reasons: Preliminary data from emission inventory questionnaires indicate that current emission factors for volatile organic compounds (VOC) are about 0.044 kg/kg of cyclohexanol/cyclohexanone produced by the cyclohexane oxidation process, and about 9.2×10^{-4} kg/kg of cyclohexanol/cyclohexanone produced by the phenol hydrogenation process. Based on the total 1976 capacity for manufacture of cyclohexanol/cyclohexanone by cyclohexane oxidation, a preliminary estimate of 15.9 Gg/yr of VOC emissions was obtained for this segment of the industry. Similarly, gross emissions of VOC resulting from the phenol hydrogenation process were estimated to be 0.11 Gg/yr.

Cyclohexanol is a colorless, crystalline solid at normal room conditions (21.1°C and 101.3 kPa), but cyclohexanone is a colorless liquid at the same conditions. Solutions of cyclohexanone and cyclohexanol may be solids or liquid at ambient conditions, depending on the relative amounts of each constituent. Other pertinent physical property data for cyclohexanol and cyclohexanone are given in Appendix A.

B. CYCLOHEXANOL/CYCLOHEXANONE USAGE AND GROWTH

Cyclohexanol/cyclohexanone is used largely for the manufacture of adipic acid and caprolactam. Adipic acid is a monomer for nylon 6,6 and a raw material for manufacture of its co-monomer, hexamethylenediamine. Caprolactam is the sole monomer for the production of nylon 6.

Current overall capacity for cyclohexanol/cyclohexanone is 1147 Gg/yr.[2] Reported production data are believed to be understated,[2] but based on adipic acid plant capacity, production, and growth[1] it is estimated that 1979 production was 1065 Gg of combined cyclohexanol/cyclohexanone and that growth will be 1—2% per annum through 1984.*

More than 90% of the cyclohexanol produced domestically is used in the manufacture of adipic acid, which is consumed primarily for nylon 6,6. The remainder of the cyclohexanol produced is used in applications other than nylon, such as the use of cyclohexanol as a stabilizer and dye solvent in the textile industry and for manufacture of phthalate esters for use in plasticizers.[2]

Approximately 95% of the cyclohexanone produced is consumed in caprolactam manufacture for nylon 6 and is oxidized as the cyclohexanol/cyclohexanone mixture to adipic acid. Use as a solvent accounts for the remainder of the cyclohexanone produced.[2]

C. DOMESTIC PRODUCERS

There are seven companies producing cyclohexanol/cyclohexanone, with a combined capacity of 1147 Gg/yr for nine plants.[2] About 80% of the capacity is based on the oxidation of cyclohexane and the remainder on hydrogenation of phenol. Table II-1 lists cyclohexanol/cyclohexanone producers, their plant locations, production capacities, and the basic raw material. Figure II-1 shows the plant locations on a map.

Companies producing cyclohexanol/cyclohexone are the following:

1. Allied Chemical Corp. produces mainly cyclohexanone, which is used captively in the production of caprolactam. A palladium catalyst is used for hydrogenation of captive phenol. Cyclohexanone and cyclohexanol are separated for sale.[2,3]
2. Celanese Corp. oxidizes purchased cyclohexane, with the majority of the product used captively to produce adipic acid for nylon 6,6 fibers.
3. Dow Badische Co. oxidizes cyclohexane, and the product is used for caprolactam production.

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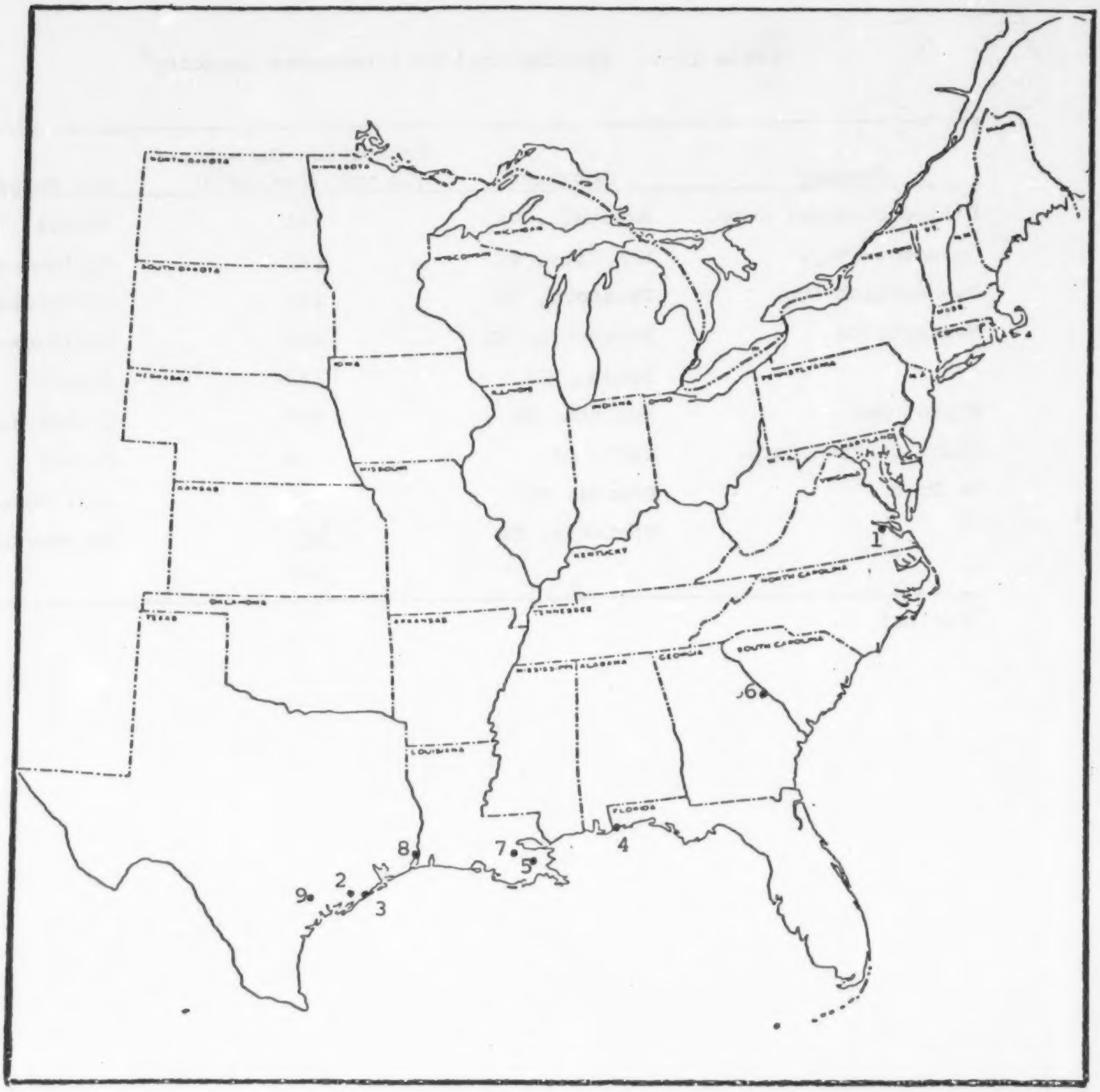
*IT Enviroscience estimate.

Table II-1. Cyclohexanol/Cyclohexanone Capacity[a]

Company	Location	Production Capacity (Gg/yr) (Jan 1979)	Raw Material
Allied Chemical Corp.	Hopewell, VA	191	Phenol
Celanese Corp.	Bay City, TX	45	Cyclohexane
Dow Badische Co.	Freeport, TX	141	Cyclohexane
Monsanto Co.	Pensacola, FL	227	Cyclohexane
	Luling, LA	23	Phenol
Nipro, Inc.	Augusta, GA	157	Cyclohexane
Union Carbide Corp.	Taft, LA	9	Phenol
Du Pont	Orange, TX	123	Cyclohexane
	Victoria, TX	231	Cyclohexane
		1147	

[a] See ref 3.



(1) Allied Chemical Corp., Hopewell, VA
(2) Celanese Corp., Bay City, TX
(3) Dow Badische Co., Freeport, TX
(4) Monsanto Co., Pensacola, FL
(5) Monsanto Co., Luling, LA
(6) Nipro, Inc., Augusta, GA
(7) Union Carbide Corp., Taft, LA
(8) Du Pont, Orange, TX
(9) Du Pont, Victoria, TX

Fig. II-1. Manufacturing Locations of Cyclohexanol/Cyclohexanone

4. Monsanto Co. at Pensacola, FL, oxidizes purchased cyclohexane, which is used for adipic and manufacture. At Luling, LA, Monsanto hydrogenates phenol to cyclohexanol, the bulk of which is converted to adipic acid at Pensacola, FA.[1]
5. Nipro, Inc., oxidizes cyclohexane, separates the cyclohexane/cyclohexanol product, dehydrogenates the cyclohexanol to cyclohexanone, and uses the cyclohexanone products to manufacture caprolactam.[4]
6. Union Carbide hydrogenates phenol and then dehydrogenates the product, followed by separation for cyclohexanone recovery and cyclohexanol recycle.[5]
7. Du Pont Co. oxidizes purchased cyclohexane; the product is used captively to produce adipic acid.[1]

D. REFERENCES*

1. Koon Ling Ring et al., "CEH Marketing Research Report on Adipic Acid," pp. 608.5031A-- 608.5031F and 608.5032A--608.5032D in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1980).

2. "CEH Salient Statistics on Cyclohexanol and Cyclohexanone," pp. 638.7020A— 638.7020D in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (January 1979).

3. F. L. Piquet, letter dated Feb. 14, 1979, to EPA from Allied Chemical, Hopewell, VA.

4. W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Nipro, Inc., Augusta, Georgia, Apr. 18, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

5. F. D. Bess, letter to EPA from Union Carbide Corp., Taft, LA, May 5, 1978, in response to EPA request for information on the cyclohexanol/cyclohexanone process.

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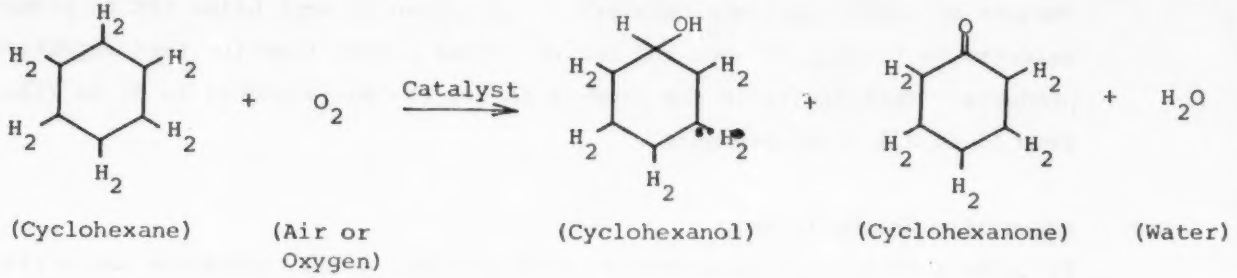
*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTIONS

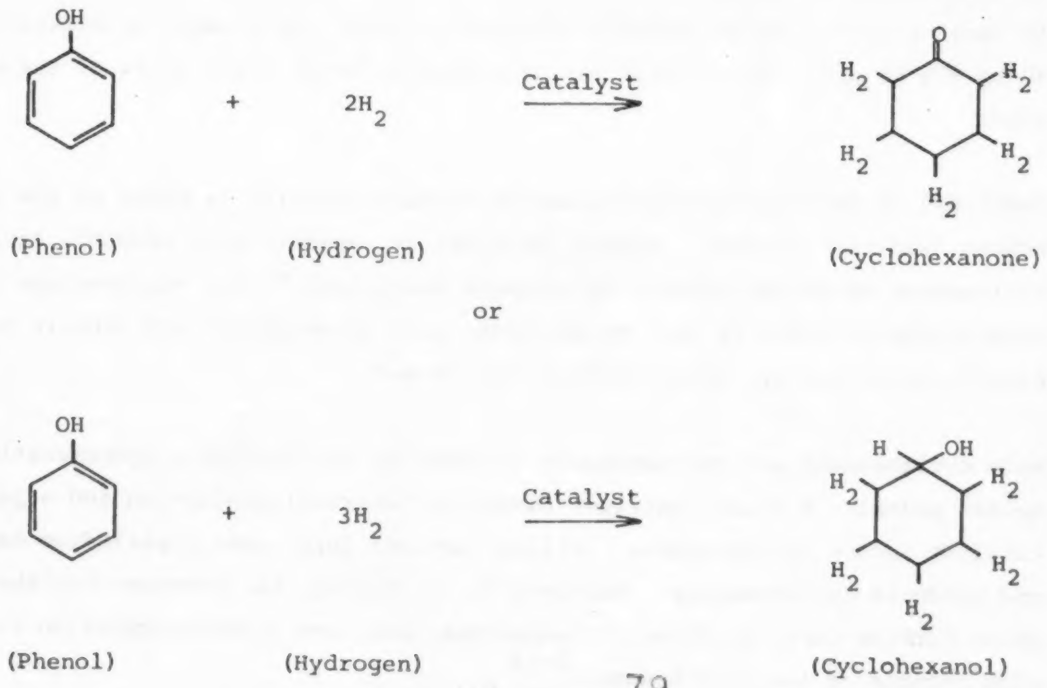
A. INTRODUCTION

Two basic processes, cyclohexane oxidation and phenol hydrogenation, are currently utilized industrially for domestic production of cyclohexanol and cyclohexanone.

Cyclohexane Oxidation Process[1] (reaction not balanced):


H2
H2
H2
H2
H2
H2
+
O2
Catalyst
H
OH
+
O
+
H2O
(Cyclohexane)
(Air or Oxygen)
(Cyclohexanol)
(Cyclohexanone)
(Water)

Phenol Hydrogenation Process:[2]


OH
+
2H2
Catalyst
O
H2
(Phenol)
(Hydrogen)
(Cyclohexanone)
or
OH
+
3H2
Catalyst
H
OH
H2
(Phenol)
(Hydrogen)
(Cyclohexanol)

In the cyclohexane oxidation process, liquid-phase catalytic oxidation of cyclohexane yields a mixture (called KA oil) of cyclohexanol and cyclohexanone (reaction conditions: 145 to 165°C and 0.8 to 1.0 MPa). Among those producers using the cyclohexane oxidation process the main process variation is the type of catalyst employed. Variations in the cyclohexane oxidation process are briefly described below:

1. Conventional Process
   A 1:1 ratio of cyclohexanol to cyclohexanone is generated using a cobalt naphthenate or cobalt stearate catalyst. Conversion is kept below 10% to promote selectivity to cyclohexanol and cyclohexanone rather than to other oxidation products. Selectivity to the product KA oil (ketone-alcohol) is 65 to 75%, and from 35 to 25% to by-products.

2. Scientific Design Process
   By using a boric acid or metaboric acid catalyst a 12% conversion and a product selectivity of 90 to 95% KA oil are realized. The ratio of alcohol to ketone in the product is 9 or 10 to 1. Monsanto is presently the only domestic company using this process.

3. Stamicarbon Modification
   In this process a cobalt octoate catalyst is used, and product selectivity is 90 to 95% KA oil. The process was developed by Dutch State Mines of the Netherlands.

About 80% of cyclohexanol/cyclohexanone product capacity is based on the cyclohexane oxidation process. Future increases in capacity will probably favor cyclohexane oxidation because cyclohexane costs less.[2] One disadvantage of this synthesis route is that by-products, such as monobasic and dibasic carboxylic acids and cyclohexyl esters, are formed.

Both cyclohexanol and cyclohexanone are made by the catalytic hydrogenation of molten phenol. A nickel catalyst favors cyclohexanol production and a palladium catalyst favors cyclohexanone. Allied Chemical Corp. uses a palladium catalyst and produces cyclohexanone. Monsanto Co. at Luling, LA, produces cyclohexanol. Union Carbide Corp. produces cyclohexanone, but uses a dehydrogenation step plus recycle of the cyclohexanol.[2--4]

Fewer by-products, are produced by the phenol hydrogenation process than by cyclohexane oxidation; it should be noted, however, that benzene is among the by-products that are formed. Also, phenol hydrogenation is much more selective toward the desired end product, cyclohexanol or cyclohexanone.[2,5] With a nickel catalyst, selectivity to cyclohexanol is typically 97 to 99%. To minimize product purification requirements, sufficient reactor residence time is allowed to permit 99+% conversion of phenol to product.[2,6]

B. CYCLOHEXANE OXIDATION PROCESS

Figure III-1 is a flow diagram illustrating the model plant* for the manufacture of cyclohexanol/cyclohexanone by cyclohexane oxidation. The process illustrated is basically conventional.[6--8]

Production of cyclohexanol/cyclohexanone begins in the oxidation reactor. Cyclohexane (Stream 1) is preheated and combined with the catalyst (Stream 2) before it enters the multistaged tower oxidation reactor. Compressed air is preheated and fed to the reactor (Stream 3). Cyclohexanol/cyclohexanone (KA oil) product from the reactor (Stream 4) is collected in a receiver. The product (Stream 5) then enters a neutralization reactor, in which carboxylic acid by-products are neutralized. The organic and aqueous phases are then separated. KA oil product (Stream 6) is sent to a stripping column for removal of cyclohexane. The aqueous phase (Stream 7), which contains carboxylic acid salts, is stripped of organics prior to storage, and is either sold or thermally oxidized. Recovered cyclohexane (Stream 8) from the stripping column is recycled for another pass through the oxidation reactor. KA oil product (Stream 9) from the bottom of the stripping column enters a KA oil recovery column. Residue from the KA recovery column (Stream 10) is thermally oxidized. Overhead product from the column (Stream 11) goes to a phase separator. The oil phase (Stream 12) is removed and then sent to a reactor for saponification of cyclohexyl esters with caustic. The caustic is removed from the KA oil product by a water wash. Crude KA oil product (Stream 13) is removed from the extraction column. Depending on the end use, the product may be further purified or be used directly as a reactant in another process, such as nitric acid oxidation of the KA oil to adipic acid. The aqueous phase (Stream 14) from the extraction column is recycled to the neutralization reactor.

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*See page I-2 for a discussion of model plants.

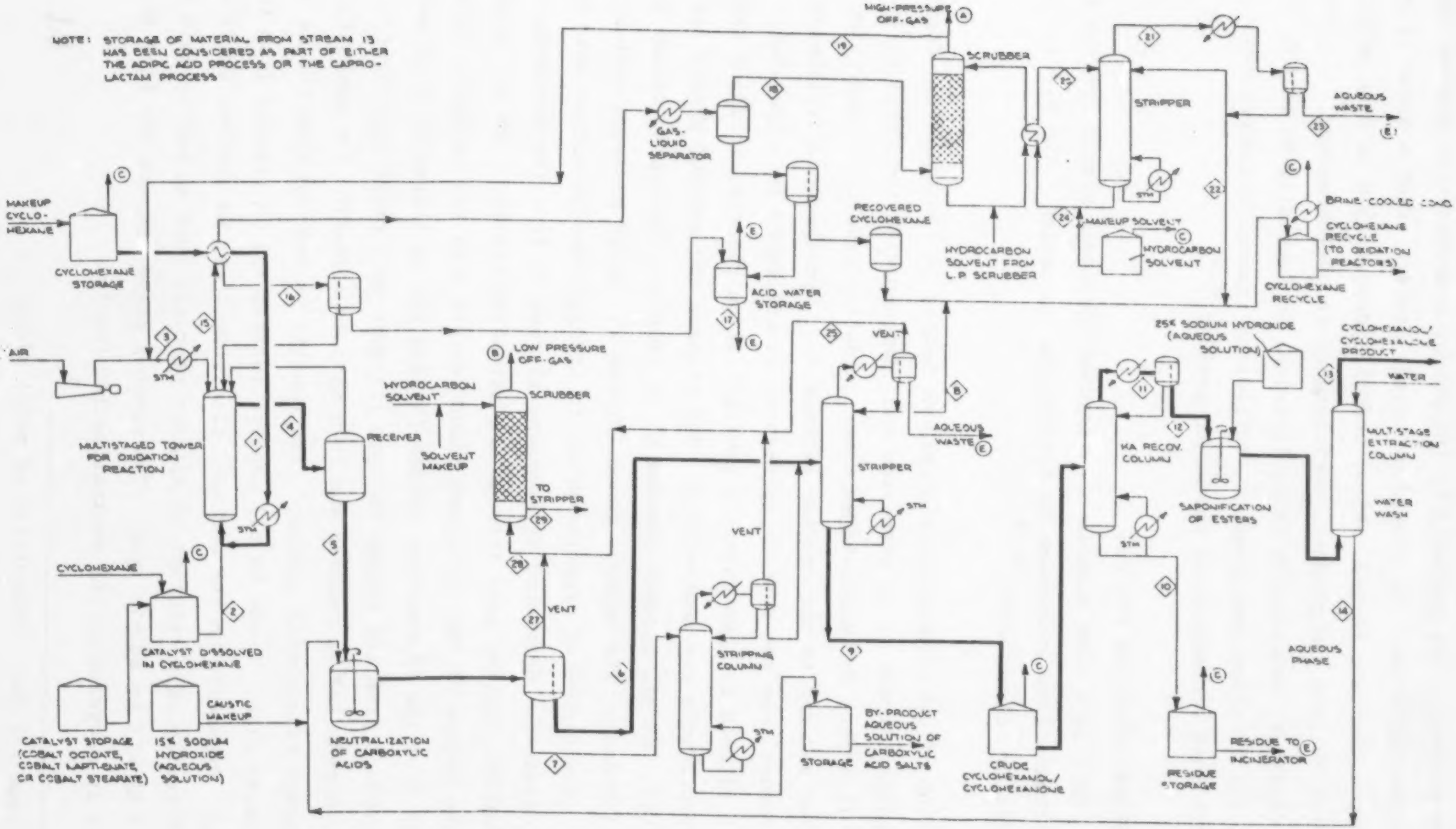
NOTE: STORAGE OF MATERIAL FROM STREAM 13 HAS BEEN CONSIDERED AS PART OF EITHER THE ADIPIC ACID PROCESS OR THE CAPROLACTAM PROCESS
MAKEUP CYCLOHEXANE
CYCLOHEXANE STORAGE
AIR
STM
MULTISTAGED TOWER FOR OXIDATION REACTION
CYCLOHEXANE
CATALYST DISSOLVED IN CYCLOHEXANE
CATALYST STORAGE (COBALT OCTOATE, COBALT NAPTHENATE OR COBALT STEARATE)
15% SODIUM HYDROXIDE (AQUEOUS SOLUTION)
CAUSTIC MAKEUP
NEUTRALIZATION OF CARBOXYLIC ACIDS
RECEIVER
GAS-LIQUID SEPARATOR
ACID WATER STORAGE
RECOVERED CYCLOHEXANE
LOW PRESSURE OFF-GAS
HYDROCARBON SOLVENT
SOLVENT MAKEUP
SCRUBBER
TO STRIPPER
VENT
STRIPPING COLUMN
STORAGE
BY-PRODUCT AQUEOUS SOLUTION OF CARBOXYLIC ACID SALTS
STRIPPER
AQUEOUS WASTE
HIGH-PRESSURE OFF-GAS
HYDROCARBON SOLVENT FROM L.P. SCRUBBER
MAKEUP SOLVENT
HYDROCARBON SOLVENT
CYCLOHEXANE RECYCLE
BRINE-COOLED COND.
CYCLOHEXANE RECYCLE (TO OXIDATION REACTORS)
CRUDE CYCLOHEXANOL/CYCLOHEXANONE
KA RECOV. COLUMN
RESIDUE STORAGE
RESIDUE TO INCINERATOR
25% SODIUM HYDROXIDE (AQUEOUS SOLUTION)
SAPONIFICATION OF ESTERS
CYCLOHEXANOL/CYCLOHEXANONE PRODUCT
WATER
MULT-STAGE EXTRACTION COLUMN
WATER WASH
AQUEOUS PHASE
A
B
C
E
1
2
3
4
5
6
7
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Fig. III-1. Process Flow Diagram for Uncontrolled Model Plant Producing Cyclohexanol/Cyclohexanone by Cyclohexane Oxidation

Off-gas vented from the cyclohexane oxidation reactor (Stream 15) is cross-exchanged with cyclohexane feed for heat recovery. Organics condensing from the gas stream (Stream 16) enter a phase separator, where the oil phase is separated and recycled to the reactor. The aqueous phase is combined with other aqueous waste (acid water storage) and leaves the system (Stream 17). Nitrogen and other gases (Stream 18) leaving the gas-liquid separator pass through a scrubber for additional cyclohexane recovery. Part of the high-pressure off-gas leaving the scrubber is recycled as diluent to compressed air supplied to the cyclohexane oxidation reactor (Stream 19); the remainder is vented (vent B). Cyclohexane and absorption solvent (Stream 20) enter a stripper for removal of cyclohexane and water as overhead product (Stream 21). This overhead product enters a phase separator for separation of the cyclohexane, which is then recycled to the system (Stream 22). The aqueous phase leaves the system as an aqueous waste stream (Stream 23). Bottoms from the stripping column (Stream 24) are recycled to the scrubber.

Off-gas from the phase separators (Streams 25, 26, and 27) is combined and is sent to a scrubber for removal of cyclohexane (Stream 28). The low-pressure off-gas is discharged at vent B. Hydrocarbon solvent, containing cyclohexane, is sent to a stripper for cyclohexane recovery (Stream 29).

C. PHENOL HYDROGENATION PROCESS

1. Model System

Figure III-2 is a very simplified flow diagram for the manufacture of cyclohexanol/cyclohexanone by the hydrogenation of phenol. It shows the three basic steps of phenol purification, catalytic hydrogenation, and product distillation of the crude reaction product. Actual production facilities can differ significantly from this diagram, especially in the number and sequence of distillation units and in additional process steps, such as dehydrogenation. In general, the emission sources should be similar.

There are three potential emission sources indicated on the diagram: the reactor off-gas from the hydrogenation step (vent A), the distillation column vacuum source vents (vents B), and the storage tank vents (vents C). There are two organic residue streams that could be sources of secondary emissions: the

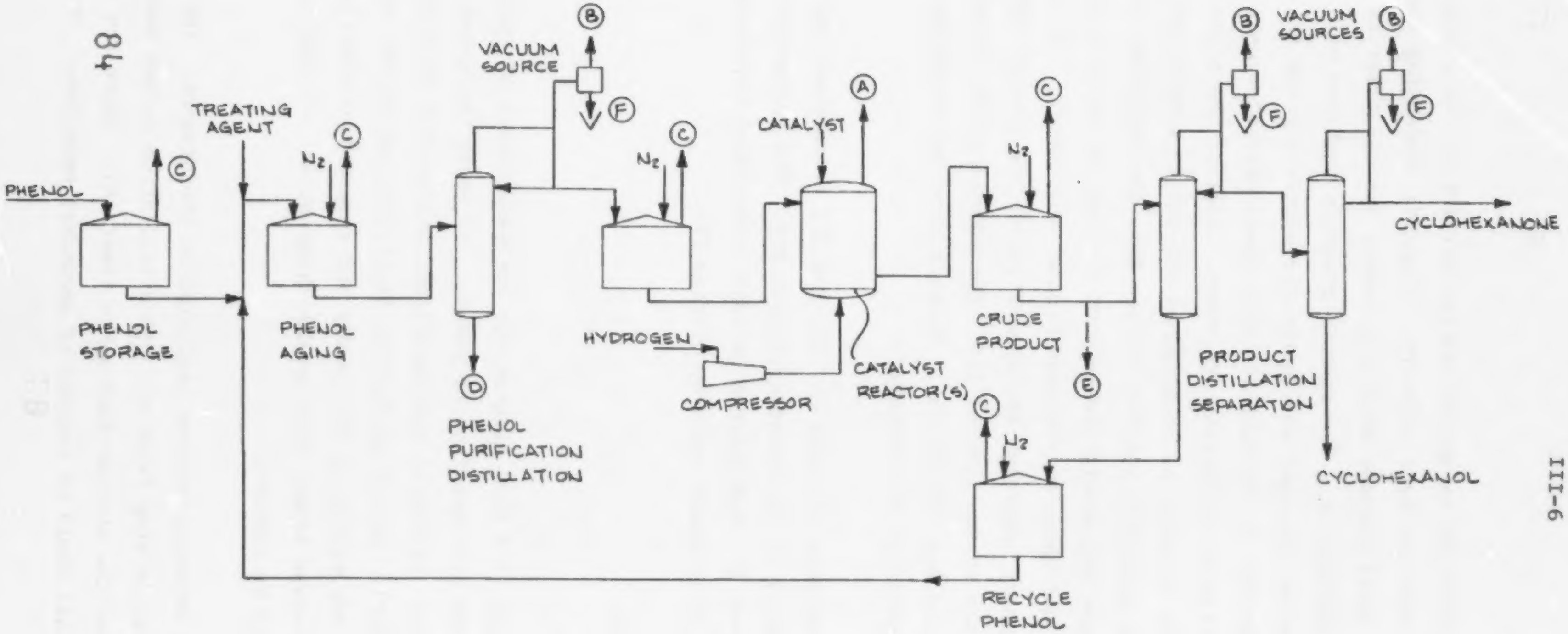
PHENOL
C
PHENOL STORAGE
TREATING AGENT
N2
C
PHENOL AGING
VACUUM SOURCE
B
F
D
PHENOL PURIFICATION DISTILLATION
N2
C
HYDROGEN
COMPRESSOR
CATALYST
A
CATALYST
REACTOR(S)
N2
C
CRUDE PRODUCT
E
C
N2
RECYCLE PHENOL
B
VACUUM SOURCES
B
F
F
PRODUCT DISTILLATION SEPARATION
CYCLOHEXANONE
CYCLOHEXANOL

Fig. III-2. Process Flow Diagram for Uncontrolled Model Plant Producing Cyclohexanone/Cyclohexanol by Phenol Hydrogenation

phenol purification distillation bottoms (Stream D) and the residues from catalyst recovery (Stream E). Sources of contaminated process waters that could be sources of secondary emissions are the wastewaters from the distillation vacuum sources (Streams F).

2. Process Variations

Allied Chemical Corp. uses a paladium catalyst that produces essentially cyclohexanone directly,[4] and the simplified diagram most nearly depicts this variation.

Union Carbide Corp. evidently uses a catalyst that gives a mixed cyclohexanol/cyclohexanone product. The crude product is dehydrogenated to give mainly cyclohexanone, and the unconverted cyclohexanol is recycled. Phenol feed purification is not practiced.[9]

Monsanto at Luling, LA, is reported tc be producing cyclohexanol.[3]

D. REFERENCES*

1. Faith, Keyes, and Clark, Industrial Chemicals, 4th ed., Wiley-Interscience, New York, 1975.

2. Koon Ling Ring, "CEH Marketing Research Report on Adipic Acid," pp. 608.5031 A--608.5032 F in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1980).

3. Amin Khalil Rafie, "Cyclohexanol and Cyclohexanone Salient Statistics," pp. 638.7020 A--638.7020 D in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (January 1979).

4. F. L. Piquet, letter to EPA from Allied Chemical, Hopewell, VA, February 14, 1979.

5. R. F. Bradley, "CEH Marketing Research Report on Caprolactam," pp. 625.2031 A--625.2032 W in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (July 1977).

6. D. E. Danby and C. R. Campbell, "Adipic Acid," pp. 510--531 in Kirk-Othmer Encyclopedia of Chemical Technology, 3d ed., vol. 1, M. Grayson et al, editors, Wiley, New York, 1978.

7. V. D. Luedeke, "Adipic Acid," pp. 129-146 in Encyclopedia of Chemical Processing and Design, vol. 2, edited by McKetta and Cunningham, Dekker Publishing Co., New York, 1971.

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9. F. D. Bess, Union Carbide Corp., letter to EPA, Taft, LA, May 5, 1978, in response to EPA request for information on the cyclohexanol/cyclohexanone process.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. CYCLOHEXANE OXIDATION PROCESS

1. Model Plant

The model plant for the cyclohexane oxidation process for manufacture of cyclohexanol/cyclohexanone (Fig. III-1) has a capacity of 100 Gg/yr, based on an annual operation of 8760 hr.* Although not an actual operating plant, it has a capacity corresponding to that of the average size process train currently being employed in cyclohexanol/cyclohexanone manufacture and represents current technology for manufacture of the product. The cyclohexane oxidation process is the most widely used process for manufacture of cyclohexanol/cyclohexanone.

Storage tank requirements are discussed under "Storage Emissions." Characteristics of the model plant that are important in air-dispersion modeling are given in Table B-1, Appendix B.

2. Sources and Emissions

a. General -- Emission rates and sources for the model plant for manufacture of cyclohexanol/cyclohexanone by cyclohexane oxidation are summarized in Table IV-1. Emissions are classified as process, storage and handling, secondary, and fugitive.

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*Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

Table IV-1. Uncontrolled Emissions from Model Plant Cyclohexane Oxidation Process

Emission Source	Stream Designation (Fig. III-1)	Emissions: Rate (kg/hr) Total VOC	Emissions: Rate (kg/hr) CO	Emissions: Ratio[a] (kg/kg) Total VOC	Emissions: Ratio[a] (kg/kg) CO
High-pressure scrubber vent	A	193	486	1.69×10^{-2}	4.26×10^{-2}
Low-pressure scrubber vent	B	30.1	111	2.64×10^{-3}	9.72×10^{-3}
Storage and handling	C	9.6		8.41×10^{-4}	
Fugitive	D	19.6		1.72×10^{-3}	
Secondary	E	1.04		9.11×10^{-5}	
Total		253	597	2.22×10^{-2}	5.23×10^{-2}

[a] kg of emission per kg of cyclohexanol/cyclohexanone produced.

Data contained in trip reports, in the GCA report,[3] and from responses to EPA's request for information from companies not visited constitute the basis for specification of model plant emissions.[1--7] Process emission factors for the model plant were calculated by averaging the emission-factor data from actual operating plants. Secondary VOC emissions, such as those from biological treatment ponds, were obtained from calculations based on flow rates and compositions of wastewater streams from existing plants. Storage emissions were estimated with equations given in AP-42. However, breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing-loss equation overestimates emissions.[8,9] Fugitive emission calculations were based on actual pump-count data and estimates of the number of compressors, values, and pressure-relief valves handling organic liquids or solutions of organics in the process. The factors given in Appendix C were applied to the data to calculate fugitive emissions of VOC.

b. Process Emissions -- Process emissions occur from the high-pressure and low-pressure scrubber vents (Vents A and B, Fig. III-1). Emissions from vents A and B consist of VOC and carbon monoxide (CO). The VOC emissions from these vents are mostly cyclohexane, but cyclohexanol, cyclohexanone, and other hydrocarbons are also present. The largest single VOC emission (193 kg/hr) from the model plant occurs from the high-pressure scrubber vent, and the second largest VOC emission (30.1 kg/hr) occurs from the low-pressure scrubber vent.

All cyclohexane oxidation plants are equipped with high- and low-pressure scrubbers, which are used mainly for economic reasons to recover hydrocarbons and are an integral part of the process. They are usually about 90% efficient in removing VOC, but are not regarded in this report as emission control devices.[3]

In refs. 1--6 little information is given concerning the effects of startup, shutdown, and process upsets. Comments in refs. 3 and 5 indicate that increases in emission during upset conditions are insignificant.[3--5]

c. Fugitive Emissions -- Process pumps, process valves, and pressure-relief valves handling VOC are sources of fugitive emissions. The model plant for cyclohexane oxidation is estimated to have 75 pumps, 1900 process valves, and 55 pressure-relief valves handling VOC. The pumps and process valves are assumed to be used 50% in light-liquid service and 50% in heavy-liquid service. The relief valves are assumed to be used 50% in vapor service and 50% in light-liquid service. The fugitive-emission factors in Appendix C were applied to this valve and pump count to determine the fugitive emissions given in Table IV-1.

d. Storage and Handling -- Virtually no emissions result from handling cyclohexanol/cyclohexanone since it is used captively. Model-plant storage emission sources are shown on the flow diagram (Fig. III-1, Source C). A list of model-plant storage tanks is given in Table IV-2. Estimates of storage tank sizes, turnovers per year, and bulk liquid temperature were influenced by the data in refs. 6 and 7. Uncontrolled emissions calculated in Table IV-1 are based on fixed-roof tanks, half full, and a 11°C diurnal temperature variation.

e. Secondary Emissions -- In the cyclohexane oxidation model plant secondary VOC emissions can occur from aqueous wastewater effluent and from storage and thermal oxidation of residue resulting from the KA oil recovery still (stream 10, Fig. III-1). Secondary VOC emissions from the wastewater are estimated to be 1.04 kg/hr.[10] Emissions from the wastewater are composed primarily of cyclohexane. Secondary emissions caused by storage and thermal oxidation of the residue from the KA oil recovery column are estimated to be negligible.

B. PHENOL HYDROGENATION PROCESS

1. Model Plant

The model plant for the phenol hydrogenation process for manufacture of cyclohexanol/cyclohexanone has a capacity of 100 Gg/yr, based on an annual operation of 8760 hr. Although slightly larger than the estimated average size of an actual process train, the capacity of the model plant was set at 100 Gg/yr to allow direct comparison of emission rates of cyclohexane oxidation and phenol hydrogenation model plant processes.

Raw-material and intermediate storage tank capacities were estimated for a 100-Gg/yr model plant. As in the case of the cyclohexane oxidation process, final product storage is considered to be part of either adipic acid or caprolactam manufacture and is not included in this report. Storage tank requirements are discussed under "Storage Emissions." Characteristics of the model

Table IV-2. Model Plant Storage Tank Data for Cyclohexane Oxidation Process

Storage Tank	Contents	No. of Tanks Required	Tank Size (m^3)	Turnovers Per Year	Bulk Temperature (°C)
Feed tank	Cyclohexane	1	6243	18.2	30
Intermediate storage[a]	Cyclohexane	1	35.8	6[b]	80
Intermediate storage	Cyclohexane	1	213	6[b]	68
Intermediate storage	Cyclohexanol/cyclohexanone	1	143	6[b]	127
Catalyst makeup	Catalyst in cyclohexane	1	35.8	130	24
Solvent used in scrubbers	Hydrocabon solvent	1	35.8	247	25

[a] The uncontrolled state for this tank is defined as a fixed-roof tank with vapor control by chilled brine condenser. Condenser efficiency is estimated to be 97%.

[b] These tanks operate at approximately constant level and the number of turnovers indicated is an attempt to account for slight level variations.

plant that are important in air dispersion modeling are given in Appendix B, Table B-2.

2. Sources and Emissions

a. General -- Emission rates and sources for the phenol hydrogenation model plant are summarized in Table IV-3. Comparison of Table IV-3 with Table IV-1 indicates that the total overall uncontrolled emissions for the phenol hydrogenation process are smaller than those for the cyclohexane oxidation process.

Data obtained from trip reports and from responses to EPA for information constitute the basis for specification of model plant emissions.[11,12]

b. Process Emissions -- The largest emission from the phenol hydrogenation model plant is off-gas from the hydrogenation reactor (Vent A, Fig. III-2). Nonmethane VOC emissions from vent A are composed of cyclohexanol, cyclohexanone, benzene, and other hydrocarbons. Table IV-4 gives the molar composition of this stream. The emission rate for VOC from vent A is 17.4 kg/hr, of which 0.91 kg/hr is benzene. The only other significant vent is the distillation column (Vents B, Fig. III-3).

The phenol hydrogenation reactor is equipped with a vent condenser and an entrainment separator, but these devices are an integral part of the process and are not emission control devices.[11]

The manufacturers using the phenol hydrogenation process employ different processes with different catalysts. This accounts for the differences in emissions in the reactor off-gas as reported by the manufacturers.[11,12] The process emissions in Table IV-3 are based on the largest producer.[12]

Process upsets, startups, and shutdowns do not appreciably increase process air emissions from vent A.[11,12] Startup of the phenol columns increases emissions slightly, because the columns operate under vacuum and the gas in the column must be removed until normal operating pressure is obtained. The volume of gas ejected is approximately equal to the internal volume of the distillation column.[12]

Table IV-3. Benzene and VOC Uncontrolled Emissions from Model Plant -- Phenol Hydrogenation Process

Emission Source	Stream Designation (Fig. III-2)	Emissions Rate (kg/hr) Benzene	Emissions Rate (kg/hr) Total VOC	Emissions Ratio[a] (kg/kg) Benzene	Emissions Ratio[a] (kg/kg) Total VOC
Hydrogenation reactor vents	A	0.91	17.4	7.97×10^{-5}	1.52×10^{-3}
Distillation vents	B		0.67		5.87×10^{-5}
Storage and handling	C		0.36		3.15×10^{-5}
Fugitive	D		5.0		4.38×10^{-4}
Secondary[b]	E				
Total		0.91	23.4	7.97×10^{-5}	2.05×10^{-3}

[a] kg of emission per kg of cyclohexanol/cyclohexanone produced.

[b] Considered to be negligible.

Table IV-4. Molar Composition of the Hydrogenation Reactor Vent -- Phenol Hydrogenation Process[a]

Component	Composition (mole %)
Cyclohexanone	0.0916
Cyclohexanol	0.0027
Cyclohexane	0.0028
Phenol	0.0006
Benzene	0.0059
Other[b]	99.90
Total	100.00

[a] See ref 12.

[b] Includes methane and other gases, such as hydrogen, which do not comprise VOC.

c. Fugitive Emissions -- The model plant is estimated to have 75 pumps, 1000 process valves, and 20 pressure-relief valves handling VOC. The pumps and process valves are assumed to be in heavy-liquid service and the pressure-relief valves in vapor service. The fugitive-emission factors shown in Appendix C were applied to this valve and pump count to determine the fugitive emissions given in Table IV-3.

d. Storage and Handling Emissions -- Comparison of the data in Tables IV-1 and IV-3 indicates that uncontrolled storage and handling losses from the phenol hydrogenation model plant are much smaller than the corresponding losses from the cyclohexane oxidation process. High volatility of cyclohexane, as opposed to the low volatility of phenol, is a major factor in this case.

Model-plant storage emission sources are shown on the flow diagram (Fig. III-2, Source B). A list of model-plant storage tanks is given in Table IV-5. Estimates of storage tank sizes, turnovers per year, and bulk liquid temperature were influenced by the data given in refs. 11 and 12. Uncontrolled storage emissions for the tanks listed in Table IV-5 are based on fixed-roof tanks, half full, and a 11°C diurnal temperature variation.

e. Secondary Emissions -- Secondary VOC emissions can result from wastewater effluent generated during hydrogenation catalyst reactivation and from the vacuum ejector on the phenol stills. Also, some waste organic tars from the phenol hydrogenation (resulting from catalyst reactivation) and phenol purification operations are disposed of by transfer to a waste treatment system. If the treatment system is a biological treatment pond, some VOC air emissions may occur from the pond. Total secondary air emissions from the phenol hydrogenation model plant are estimated to be negligible.[10]

Table IV-5. Model Plant Storage Tank Data
Phenol Hydrogenation Process

Storage Tank	Contents	No. of Tanks Required	Tank Size (m^3)	Turnovers per Year	Bulk Temperature (°C)
Feed	Phenol	1	4654	18.2	60
Phenol aging	Phenol	1	143	6*	60
Phenol purified	Phenol	1	143	6*	60
Phenol recycle	Phenol	1	143	6*	60
Crude product	Cyclohexanol/ cyclohexanone	1	284	6*	45

[*] These tanks operate at approximately constant level, and the number of turnovers indicated reflects an attempt to account for slight level variations.

C. REFERENCES*

1. Celanese Chemical Company, letter dated Apr. 21, 1978, in response to EPA's request for information on emissions data on cyclohexanol/cyclohexanol and adipic acid production facilities.

2. Dow Badische Company, letter dated May 12, 1978, in response to EPA's request for information on emissions data on cyclohexanol/cyclohexanone and caprolactam producton facilities.

3. D. R. Durocher et al., Screening Study to Determine Need for Standards of Performance for New Adipic Acid Plants. Final Report, GCA-TR-76-16-G (July 1976).

4. Du Pont Company, letter dated Apr. 12, 1978, in response to EPA's request for information on emissions data on cyclohexanol/cyclohexanone and adipic acid production facilities.

5. W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Monsanto Textiles Company, Pensacola, FL, Feb. 8, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

6. W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Nipro, Inc., Augusta, GA, Apr. 18, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

7. Dow Badische Comany, emissions data in Emissions Inventory Questionnaire submitted to Texas Air Control Board, Mar. 19, 1976.

8. C. C. Masser, "Storage of Petroleum Liquids," Sect. 4.3 in Supplement No. 7 for Compilation of Air Pollutant Emission Factors, AP-42, 2d ed., EPA, Research Triangle Park, NC (April 1977).

9. E. C. Pulaski, TRW, Inc., letter dated May 30, 1979, to R. Burr, EPA.

10. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

11. Union Carbide Corporation, letter dated May 5, 1978, in response to EPA's request for information on emissions data on cyclohexanol/cyclohexanone production facilities.

12. W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Allied Chemical Company, Hopewell, VA, Feb. 21, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. CYCLOHEXANE OXIDATION PROCESS

1. Process Emissions

Emissions of VOC and CO occur from the high-pressure and low-pressure scrubbers, as indicated in Table IV-1. Information from manufacturers indicates that in one case a flare is used as a control device and in another only the high-pressure emission is fed to an existing boiler.[1--7]

The vent gases from the scrubbers can be thermally oxidized to effectively control the VOC and CO in them; however, because of the large percentage of nitrogen and other noncombustible gases normally present, supplemental fuel must be added to ensure proper combustion. For the model plant the high-pressure and low-pressure scrubber emissions (Vents A and B, Fig. III-1) are assumed to be processed in a single thermal oxidizer with a reduction of 99% in VOC and CO emissions when operating at 871°C and 0.75-sec residence time.[8] The controlled emission values are given in Table V-1.

In addition to a thermal oxidizer the scrubber's vent gas emissions could be controlled equally effectively by feeding them to an existing boiler[9] or by using a catalytic oxidizer.[10] These control systems could have special attractions, especially in retrofit situations. In using an existing boiler the high-pressure vent, which is an order of magnitude larger, has sufficient pressure to transport the emissions to the use site. The low-pressure vent may need compression or special controls to be handled. A cyclohexanol/cyclohexanone and adipic acid plant requires a large amount of steam.[7] A catalytic oxidizer used on the high-pressure vent could be combined into a system using a power recovery turbine, thereby resulting in a significant energy savings.[11]

2. Fugitive Emissions

Controls for fugitive emissions from the synthetic organic chemicals manufacturing industry are discussed in a separate EPA document.[12] Emissions from pumps, process valves, and pressure-relief devices can be controlled by an appropriate leak-detection system and with repair and maintenance as needed. Controlled fugitive emissions were calculated with the appropriate factors given in Appendix C and are included in Table V-1.

Table V-1. Controlled Emissions from Model Plant Using Cyclohexane Oxidation Process

Emission Source	Vent or Source Designation (Fig. III-1)	Control Device or Technique	Emission Reduction (%)	Emissions Rate (kg/hr) VOC	Emissions Rate (kg/hr) CO	Emissions Ratio[a] (kg/kg) VOC	Emissions Ratio[a] (kg/kg) CO
High-pressure scrubber vent	A	Thermal oxidizer	99	1.93	4.86	1.69×10^{-4}	4.26×10^{-4}
Low-pressure scrubber vent	B	Thermal oxidizer	99	0.30	1.11	2.64×10^{-5}	9.72×10^{-5}
Storage and handling	C	Internal floating roof on cyclohexane tanks	85	1.80		1.55×10^{-4}	
Fugitive	D	Detection and repair of major leaks		6.90		6.04×10^{-4}	
Secondary	E	None		1.04		9.11×10^{-5}	
Total				11.97	5.97	1.05×10^{-3}	5.23×10^{-4}

[a] kg of emission per kg of cyclohexanol/cyclohexanone produced.

3. Storage and Handling Emissions

Options for control of storage emissions are covered in another EPA report.[13] Emissions listed in Table V-1 are based on the assumption that only the large cyclohexane storage tank and one of the cyclohexane intermediate tanks (Table IV-2) are fitted with contact-type internal floating roofs* with secondary seals. This is estimated to reduce fixed-roof-tank emissions by 85%.[14]

4. Secondary Emissions

No control system has been identified for secondary emissions from the model plant. Control of secondary emissions is discussed in another EPA report.[15]

B. PHENOL HYDROGENATION PROCESS

1. Process Emissions

Emissions of VOC, including benzene, occur from the hydrogenation reactor, as indicated in Table IV-3. Information from cyclohexanol/cyclohexanone manufacturers using the phenol hydrogenation process indicates that the only type of control technique in use for emissions from these vents consists of burning the reactor off-gas in a boiler.[16]

For the phenol hydrogenation model plant it is assumed that the hydrogenation reactor off-gas is used as a fuel gas. When the off-gas is used as a fuel, the VOC destruction efficiency can be greater than 99.9%.[9] The controlled emission value is given in Table V-2.

Control method alternatives that have been suggested are carbon adsorption, refrigeration condensation, and cyrogenic separation.[17] These methods may have application in specific cases and would have the advantage that contained hydrogen and organics could be recovered for recycle.

2. Fugitive Emissions

Controls for futitive emissions from the synthetic organic chemical manufacturing industry are discussed in a separate EPA document.[12] Emissions from pumps, process valves, and pressure relief devices can be controlled by an appropriate

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*Consist of internal floating covers or covered floating roofs as defined in API 25-19, 2d ed., 1976 (fixed-roof tanks with internal floating device to reduce vapor loss).

Table V-2. Controlled Emissions from Model Plant -- Phenol Hydrogenation Process

Emission Source	Vent or Source Designation (Fig. III-2)	Control Device or Technique	Emission Reduction (%)	Emissions			
				Rate (kg/hr)		Ratio[a] (kg/kg)	
				Total VOC	Benzene	Total VOC	Benzene
Hydrogenation reactor vent	A	Route to plant fuel gas supply	99.9	0.0174	0.0009	1.52×10^{-6}	7.97×10^{-8}
Distillation vents	B	Route to plant fuel gas supply	99.9	0.0007		5.87×10^{-8}	
Storage and handling	C	None		0.36		3.15×10^{-5}	
Fugitive	D	Detection and repair of major leaks		3.0		2.63×10^{-4}	
Secondary[b]	E	None					
Total				3.38	0.0009	2.96×10^{-4}	7.97×10^{-8}

[a] kg of emission per kg of cyclohexanol/cyclohexanone produced.

[b] Considered to be negligible.

leak-detection system and with repair and maintenance as needed. Controlled fugitive emissions were calculated with the appropriate factors given in Appendix C and are included in Table V-2.

3. Storage and Handling Sources

Options for control of storage emissions are covered in another EPA report.[13] For the model plant no controls for storage are assumed.

4. Secondary Emissions

No control system has been identified for the model plant. Control of secondary emissions is discussed in another EPA report.[15]

C. REFERENCES*

1. Celanese Chemical Company, letter dated Apr. 21, 1978, in response to EPA's request for information on emissions data on cyclohexanol/cyclohexanol and adipic acid production facilities.

2. Dow Badische Company, letter dated May 12, 1978, in response to EPA's request for information on emissions data on cyclohexanol/cyclohexanone and caprolactam production facilities.

3. D. F. Durocher *et al*., *Screening Study to Determine Need for Standards of Performance for New Adipic Acid Plants. Final Report*, GCA-TR-76-16-G (1976).

4. Du Pont Company, letter dated Apr. 12, 1978, in response to EPA's request for information on emissions data on cyclohexanol/cyclohexanone and adipic acid production facilities.

5. W. D. Bruce, IT Enviroscience, Inc., *Trip Report for Visit to Monsanto Textiles Company, Pensacola, FL, Feb. 8, 1978* (on file at EPA, ESED, Research Triangle Park, NC).

6. W. D. Bruce, IT Enviroscience, Inc., *Trip Report for Visit to Nipro, Inc., Augusta, GA, Apr. 18, 1978* (on file at EPA, ESED, Research Triangle Park, NC).

7. W. R. Chalker, E. I. du Pont de Nemours & Company, Inc., letter to EPA with information on cyclohexanol/cyclohexanone process, March 12, 1979.

8. J. W. Blackburn, IT Enviroscience, Inc., Control *Device Evaluation. Thermal Oxidation*, (July 1980) (EPA/ESED report, Research Triangle Park, NC).

9. V. Kalcevic, IT Enviroscience, Inc., *Control Devices Evaluation. Flares and the Use of Emission as Fuels* (in preparation for EPA, ESED, Research Triangle Park, NC) (August 1980).

10. J. A. Key, IT Enviroscience, Inc., *Control Device Evaluation. Catalytic Oxidation* (October 1980) (EPA/ESED report, Research Triangle Park, NC).

11. C. J. Schaefer and T. M. Kenesson, Celanese Chemical Co., Inc., letter to the EPA with information on cyclohexanol/cyclohexanone process, January 12, 1979.

12. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., *Fugitive Emissions* (September 1980) (EPA/ESED report, Research Triangle Park, NC).

13. D. G. Erikson, IT Enviroscience, Inc., *Storage and Handling* (September 1980) (EPA/ESED report, Research Triangle Park, NC).

14. W. T. Moody, TRW, Inc., letter dated Aug. 15, 1979, to Dave Beck, EPA.

15. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Icn., *Secondary Emissions* (September 1980) (EPA/ESED report, Research Triangle Park, NC).

16. Union Carbide Corporation, letter dated May 5, 1978, in response to EPA's request for information on emissions data on cyclohexanol/cyclohexanone production facilities.

17. F. L. Piguet, Allied Chemical, letter with information on cyclohexanol/cyclohexanone process dated Feb. 14, 1979, to EPA.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. ENVIRONMENTAL AND ENERGY IMPACTS

1. Cyclohexane Oxidation Process

Table VI-1 shows the environmental impact of reducing the total VOC emissions by application of the described control systems (Sect. V) to the model plant described in Sects. III and IV. Use of these control devices or techniques results in the reduction of total VOC emissions by 2.11 Gg/yr for the model plant and in the controlled emissions from the model plant being reduced to 0.10 Gg/yr.

a. High-Pressure and Low-Pressure Vents -- The use of a thermal oxidizer for the control of vents A and B (Fig. III-1) reduces the model-plant VOC emissions by an estimated 1.93 Gg/yr and CO emissions by 5.18 Gg/yr. The use of a thermal oxidizer requires an estimated 18.2 GJ/hr of supplemental fuel; when heat recovery by a 400-psig steam waste heat boiler is practiced, there is a net energy savings of 3.1 GJ/hr.

b. Other Emissions (Storage and Fugitive) -- These sources are controlled in the model plant by internal-floating-roof storage tanks and by detection and repair of leaking components for fugitive emissions. Application of these controls results in a VOC emission reduction of 0.18 Gg/yr for the model plant. Neither of these controls consumes significant energy, nor do they have an adverse environmental impact.

2. Phenol Hydrogenation Process

Table VI-2 shows the environmental impact of reducing the total VOC emissions by application of the described control systems (Sect. V) to the model plant described in Sects. III and IV. Use of these control devices or techniques results in the reduction of total VOC emissions by about 176 Mg/yr for the model plant and in the controlled emissions from the model plant being 29.6 mg/yr.

a. Hydrogenation Reactor Vent -- The use of the emissions from vents A and B (Fig. III-2) as fuel gases reduces the model-plant VOC emissions by an estimated 152 Mg/yr and benzene emissions by 8 Mg/yr. Using these emissions as fuel will reduce a plant's other source energy demands.

Table VI-1. Environmental Impact of Controlled Cyclohexane Oxidation Model Plant

Emission Source	Stream or Vent Designation (Fig. III-1)	Control Device or Technique	Emission Reduction (%)	Emission Reduction (Gg/yr)	
				VOC	CO
High-pressure scrubber vent	A	Thermal oxidizer	99	1.67	4.22
Low-pressure scrubber vent	B	Thermal oxidizer	99	0.26	0.96
Storage and handling	C	Internal floating roof on cyclohexane tanks	85	0.07	
Fugitive	D	Detection and repair of major leaks		0.11	
Secondary	E	None			
Total				2.11	5.18

Table VI-2. Environmental Impact of Controlled Phenol Hydrogenation Model Plant

Emission Source	Stream or Vent Designation (Fig. III-2)	Control Device or Technique	Emission Reduction (%)	Emission Reduction (Mg/yr)	
				Total VOC	Benzene
Hydrogenation reactor vent	A	Use as fuel gas	99.9	152.3	8.0
Distillation vents	B	Use as fuel gas	99.9	5.8	
Storage and handling	C	None			
Fugitive	D	Detection and repair of major leaks		17.5	
Secondary	E	None			
Total				175.6	8.0

b. Other Emissions (Fugitive) -- These sources are controlled in the model plant by detection and repair of leaking components. This results in a VOC emission reduction of 17.5 Mg/yr. This control does not consume significant energy nor have an adverse environmental impact.

B. CONTROL COST IMPACT

This section gives estimated costs and cost-effectiveness data for control of VOC emissions resulting from the production of cyclohexanol/cyclohexanone. Details of the model plants (Figs. III-1 and III-2) are given in Sects. III and IV. Cost-estimate sample calculations are included in Appendix D.

Capital cost estimates represent the total investment required to purchase and install all equipment and material required to provide a complete emission control system performing as defined for a new plant at a typical location. These estimates do not include the cost of cyclohexanol/cyclohexanone production lost during installation or startup, research and development, or land acquisition.

Bases for the annual cost estimates for the control alternatives include utilities, operating labor, maintenance supplies and labor, recovery credits, capital charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. The cost factors used are itemized in Table VI-3.

1. Cyclohexane Oxidation Process

a. Absorber Vents -- The estimated installed capital cost of a thermal oxidizer designed to reduce by 99% the VOC emissions from the high-pressure and low-pressure adsorber vents is \$500,000 when heat recovery is not used or is \$800,000 when the heat is recovered by steam being generated in a waste-heat boiler. These costs are based on a thermal oxidizer that is designed for a residence time of 0.75 sec at 871°C, is completely installed, and is equipped to burn supplemental natural-gas fuel. See Appendix D for the cost-estimate sample calculations for a thermal oxidizer, based on a complete installation as described in the control device evaluation report on thermal oxidizers.[1]

Table VI-3. Annual Cost Parameters

Operating factor	8760 hr/yr[a]
Operating labor	$15/man-hr
Fixed costs	
Maintenance labor plus materials, 6%	29% of installed capital cost
Capital recovery, 18%[b]	
Taxes, insurances, administration charges, 5%	
Utilities	
Electric power	$8.33/GJ ($0.03/kWh)
Natural gas	$1.90/GJ ($2.00/thousand ft^3 or million Btu)
Heat recovery credits (equivalent to natural gas)	$1.90/GJ ($2.00/million Btu)

[a] Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

[b] Based on 10-year life and 12% interest.

The costs are also based on the thermal oxidizer system being located within the battery limits of the production facility. If for safety or for a particular retrofit situation the oxidizer needs to be located some distance from the facility, considerable capital cost could be associated with the required additional piping.[2]

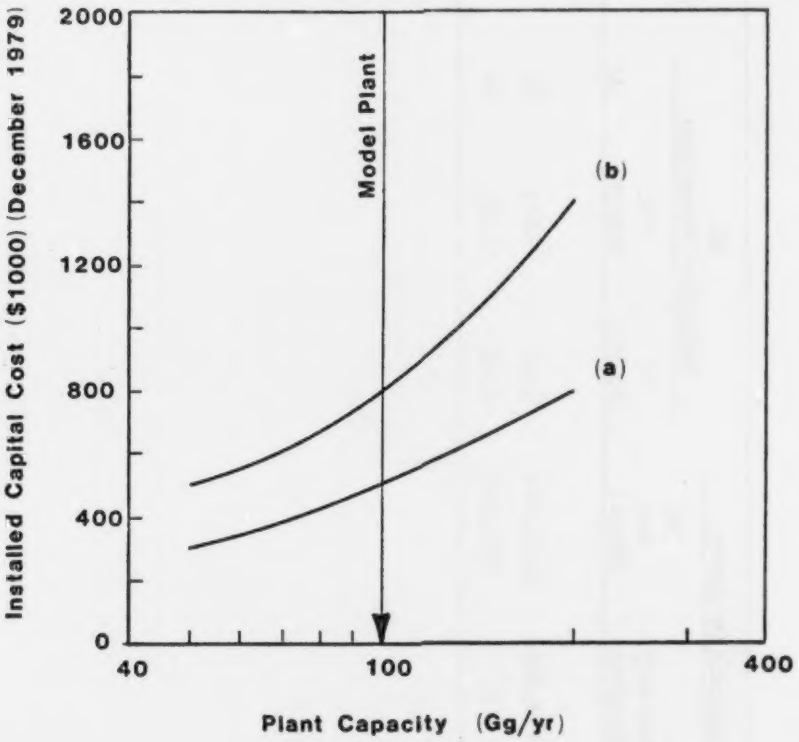
The vent gas rates vary directly with the production rate; therefore a plant with half the capacity of the model plant will require a thermal oxidizer with half the capacity of one for the model plant. Figure VI-1 was plotted to show the variation of installed capital cost of a thermal oxidizer, both without heat recovery and with a waste-heat boiler, versus plant capacity.

To determine the cost effectiveness of the thermal oxidizer, estimates were made of the gross annual operating cost for both cases: without heat recovery and with a waste-heat boiler. For the waste-heat boiler case the recovery credit and the net annual operating cost were also calculated; see Table VI-4. The variation of net annual costs with plant capacity for both cases is shown in Fig. VI-2. The cost effectiveness for each case for controlling VOC was calculated from the net annual cost and its emission reduction; see Table VI-3. The variation in cost effectiveness with plant capacity is shown in Fig. VI-3.

b. Storage -- The system for controlling storage emissions is internal-floating-roof tanks for cyclohexane storage. Another EPA report covers storage and handling emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.[3]

c. Fugitive Sources -- A control system for fugitive sources is defined in Appendix C. Another EPA report covers fugitive emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.[4]

d. Secondary Sources -- No control system has been identified for controlling the secondary emissions from the model plant.



(a) Thermal oxidizer without heat recovery

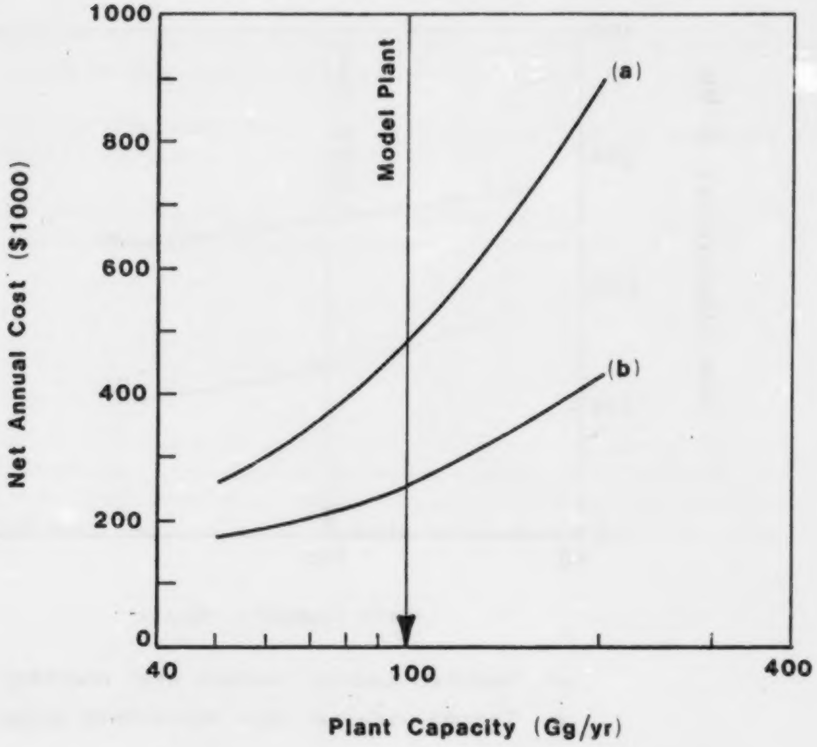
(b) Thermal oxidizer with waste-heat boiler

Fig. VI-1. Installed Capital Cost vs Plant Capacity for Emission Control (Thermal Oxidation)

Table VI-4. Emission Control Cost Estimates for Cyclohexanol/Cyclohexanone Model Plants

Control	Total Installed Capital Cost	Annual Operating Costs			(B) Emission Reduction			(C)[a] Cost Effectiveness
		Gross Annual	Recovery Credits	(A) Net Annual	CO (Mg/yr)	VOC (Mg/yr)	(%)	VOC (per Mg)
Thermal oxidizer								
With heat recovery	$800,000	$588,000	$334,000	$254,000	5180	1930	99	$132
Without heat recovery	500,000	483,000	0	483,000	5180	1930	99	250

[a] (C) = (A) ÷ (B).



(a) Thermal oxidizer without heat recovery
(b) Thermal oxidizer with waste-heat boiler

Fig. VI-2. Net Annual Cost vs Plant Capacity for Emission Control (Thermal Oxidation)

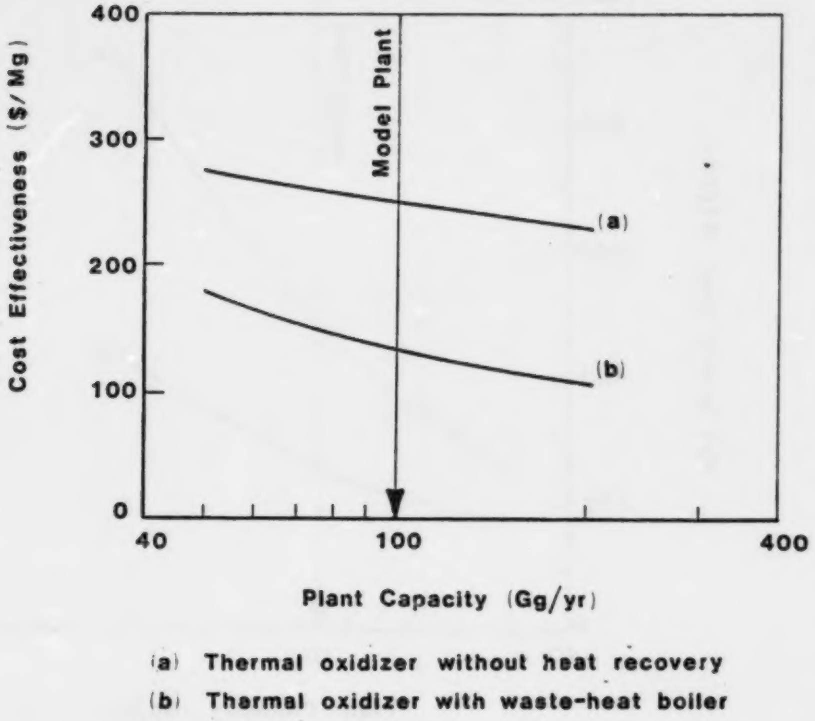


Fig. VI-3. Cost Effectiveness vs Plant Capacity for Emission Control (Thermal Oxidation)

2. Phenol Hydrogenation Process

a. Hydrogenation Reactor Vent -- Off-gas for the phenol hydrogenation (stream A, Fig. III-3) is sent to the plant fuel-gas system for combustion in a boiler. The costs associated with the use of VOC emissions as fuel are very site specific. If there is a satisfactory use for the fuel with a reasonable cost system, there can be a cost-effectiveness savings. Specific cost-effectiveness calculations were not performed.

b. Storage -- Storage emissions from the phenol hydrogenation model plant are small and no control system has been identified.

c. Fugitive Sources -- A control system for fugitive sources is defined in Appendix C. Another EPA report covers fugitive emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.[4]

d. Secondary Sources -- No control system has been identified for the secondary emissions from the model plant.

C. REFERENCES*

1. J. W. Blackburn, IT Enviroscience, Inc., Control Device Evaluation. Thermal Oxidation (July 1980) (EPA/ESED report, Research Triangle Park, NC).

2. W. R. Chalker, E. I. du Pont de Nemours & Co., Inc., letter to EPA with information on cyclohexanol/cyclohexanone process, March 12, 1979.

3. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

4. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VII. SUMMARY

Cyclohexanol/cyclohexanone are currently manufacturer by two basic processes, cyclohexane oxidation or phenol hydrogenation. The cyclohexane oxidation process produces a mixture, called KA oil, of cyclohexanol and cyclohexanone that can be used directly as a raw-material feed to an adipic acid plant. The phenol hydrogenation process can produce primarily either cyclohexanol or cyclohexanone or a mixture of the two, depending on the type of catalyst used. Each of the three producers using this process practices a different version. About 80% of the listed 1979 plant capacity is based on the cyclohexane oxidation process and 20% on the phenol hydrogenation process.

The annual growth rate of cyclohexanol/cyclohexanone manufacture is estimated to be 1—2% through 1984. The 1979 listed capacity was 1147 Gg/yr and the estimated production was 1065 Gg.

Emission sources and uncontrolled and controlled emission rates for the cyclohexane oxidation process and the phenol hydrogenation process model plants are given in Tables VII-1 and VII-2. The current VOC emissions projected for the industry based on the estimated degree of control existing in 1980 is 11,700 Mg/yr. These emission estimates are based on engineering judgement and data from individual producers, state emission control agencies, and the open literature. The following individual estimated projections were made:

Source	1980 VOC Emission (Mg/yr)
Process	10,900
Storage	140
Fugitive	580
Secondary	80
	11,700

The predominant emission points for the cyclohexane process are the high-pressure and low-pressure scrubber vents. The gases from these vents can be controlled by a thermal oxidizer, which will reduce both the VOC emissions and the CO emissions by 99%. The installed cost of a thermal oxidizer for the model plant is $500,000 without heat recovery and $800,000 with heat recovery by use of a

Table VII-1. Emission Summary for Cyclohexane Oxidation Model Plant

Emission Source	Stream or Vent Designation (Fig. III-1)	Emission Rate (kg/hr)			
		Uncontrolled		Controlled	
		VOC	CO	VOC	CO
High-pressure scrubber vent	A	193	486	1.93	4.86
Low-pressure scrubber vent	B	30.1	111	0.30	1.11
Storage and handling	C	9.6		1.80	
Fugitive	D	19.6		6.90	
Secondary	E	1.04		1.04	
Total		253	597	11.97	5.97

Table VII-2. Emission Summary for Phenol Hydrogenation Model Plant

Emission Source	Stream or Vent Designation (Fig. III-2)	Emission Rate (kg/hr)			
		Uncontrolled		Controlled	
		Benzene	Total VOC	Benzene	Total VOC
Hydrogenation reactor vent	A	0.91	17.4	0.0009	0.0174
Distillation vents	B		0.67		0.0007
Storage and handling	C		0.36		0.36
Fugitive	D		5.0		3.0
Secondary	E				
Total		0.91	23.4	0.0009	3.38

waste-heat boiler. Supplemental fuel is required. The cost effectiveness for VOC controlled is $250/Mg without heat recovery and is $132/mg with a waste heat boiler.

The predominant emission point for the phenol hydrogenation process is the hydrogenation reactor vent. This vent can be controlled by the emission being used as a fuel gas, which will reduce both the total VOC and the small quantity of contained benzene emissions by 99.9% or greater.

APPENDIX A

PHYSICAL PROPERTIES OF CYCLOHEXANOL, CYCLOHEXANONE, BENZENE, CYCLOHEXANE, AND PHENOL

Table A-1. Physical Properties of Cyclohexanol*

Synonyms	Hexahydrophenol
Molecular formula	$C_6H_{12}O$
Molecular weight	100.16
Physical state	Colorless crystalline solid
Vapor pressure	467 Pa at 34°C
Vapor specific gravity	3.46 (air = 1)
Boiling point	161.1°C
Melting Point	25.5°C
Liquid specific gravity	0.9493 at 20°C/4°C
Water solubility	3.6 wt % at 20°C

*J. Dorigan, B. Fuller, and R. Duffy, p. AI-320 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A--C), Rev. 1, Appendix I, MTR-7248, MITRE Corp., McLean, VA (September 1976).

Table A-2. Physical Properties of Cyclohexanone*

Synonyms	Pimelic ketone, anone, sextone, ketohexamethylene
Molecular formula	$C_6H_{10}O$
Molecular weight	98.14
Physical state	Colorless liquid
Vapor pressure	600 Pa at 25°C
Vapor specific gravity	No data
Boiling point	155.6°C
Melting point	-45°C
Liquid specific gravity	0.9478 at 20°C/4°C
Water solubility	50 g/l at 30°C

*J. Dorigan, B. Fuller, and R. Duffy, p. AI-322 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (A--C), Rev. 1, Appendix I, MTR-7248, MITRE Corp., McLean, VA (September 1976).

Table A-3. Physical Properties of Benzene[a]

Synonyms	Benzol, coal naphtha, phenylhydride
Molecular formula	C_6H_6
Molecular weight	78.11
Physical state	Liquid
Vapor pressure	95.9 mm Hg at 25°C
Vapor specific gravity	2.77
Boiling point	80.1°C at 760 mm Hg
Melting point	5.5°C
Liquid specific gravity	0.8787 at 20°C/4°C
Water solubility	1.79 g/liter
Octanol/water partition coefficient	2.28

[a] From: J. Dorigan, B. Fuller, and R. Duffy, "Benzene," p AI-102 in Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C), MTR-7248, Rev 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

Table A-4. Physical Properties of Cyclohexane[a]

Synonyms	Hexahydrobenzene, hexanaphthene, hexamethylene
Molecular formula	C_6H_{12}
Molecular weight	84.16
Physical state	Liquid
Vapor pressure	98.14 mm Hg at 25°C (96.97 mm Hg at 25°C)
Vapor specific gravity	2.90
Boiling point	80.7°C at 760 mm Hg
Melting point	6.3°C
Liquid specific gravity	0.77855 at 20°C/4°C
Water solubility	<1 g/liter

[a] From: J. Dorigan, B. Fuller, and R. Duffy, "Cyclohexane," p AI-318 in Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C), MTR-7248, Rev 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

Table A-5. Properties of Phenol[a]

Synonyms	Carbolic acid, phenic acid, phenylic acid, oxybenzene, phenyl hydroxide, hydroxybenzene
Molecular formula	C_6H_6O
Molecular weight	94.11
Physical state	Solid
Vapor pressure	0.530 mm Hg at 25°C
Vapor specific gravity	3.24
Boiling point	181.9°C at 760 mm
Melting point	42.5 to 43°C
Density	1.0576 g/ml at 20°C/4°C
Water solubility	Soluble

[a] From: J. Dorigan *et al.*, "Phenol," p. AIV-32 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals O-Z)*, MTR-7248, Rev 1, Appendix IV, Mitre Corp., McLean, VA (September 1976).

APPENDIX B

AIR-DISPERSION PARAMETERS

Table B-1. Air-Dispersion Parameters for Cyclohexane Oxidation Model Plant (Capacity, 100 Gg/yr), Controlled and Uncontrolled

Emission Source	Emission Rate (g/sec)	Tank Height (m)	Tank Diameter (m)	Stack Height (m)	Stack Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
				Uncontrolled Emissions				
Process emissions from low- and high-pressure scrubber vent streams combined (Vents A and B, Fig. III-1)	62			30.5	0.808			
Storage								
Feed tank	2.41	12.2	25.6			303		
Intermediate	0.006	2.44	4.33			353		
Intermediate	0.20	7.32	6.10			341		
Intermediate	0.06	2.44	4.33			297		
Catalyst makeup	0.03	7.32	5.00			400		
Solvent (scrubbers)	0.001	2.44	4.33			298		
Fugitive	5.40							
Secondary	0.29	1	83			Ambient		
				Controlled Emissions				
Process emissions from low- and high-pressure scrubber vent streams combined (Vents A and B, Fig. III-1)	0.62			30.5	0.808	533	5.13	10
Storage								
Feed tank	0.36	12.2	25.6			303		
Intermediate	None[c]	2.44	4.33			353		
Intermediate	0.03	7.32	6.10			341		
Intermediate	0.06[b]	2.44	4.33			297		
Catalyst makeup	0.03[b]	7.32	5.00			400		
Solvent (scrubbers)	0.001[b]	2.44	4.33			298		
Fugitive	1.91[b]							
Secondary	0.29[b]							

[a] Distributed over an area of 100 m by 200 m.

[b] No control specified.

[c] Vented back to process.

Table B-2. Air-Dispersion Parameters for Phenol Hydrogenation Model Plant (Capacity, 100 Gg/yr), Controlled and Uncontrolled

Source	Emission Rate (g/sec) Total VOC	Emission Rate (g/sec) Benzene	Tank Height (m)	Tank Diameter (m)	Stack Height (m)	Stack Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
			Uncontrolled Emissions						
Process emissions									
Hydrogenation reactor vent	4.83	0.253			18.3	0.305	306	2.00	27.5
Distillation vents	0.19								
Storage[a]									
Phenol feed	0.08		12.2	22.0			333		
Phenol in-process (3 tanks)	0.005		7.32	5.0			333		
Cyclohexanol cyclohexanone crude product	0.01		7.32	7.04			318		
Fugitive[b]	1.39						318—473		
			Controlled Emissions						
Process[c]	0.005	0.00025							
Fugitive[b]	0.83						318—473		

[a] No control specified.

[b] Distributed over an area of 100 m by 200 m.

[c] Combustion boiler assumed to be fueled by this stream.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

---

*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

COST-ESTIMATE SAMPLE CALCULATIONS

This appendix contains sample calculations showing how the costs presented in this report were estimated.

The accuracy of an estimate is a function of the degree of data available when the estimate was made. Figure D-1 illustrates this relationship. The contingency allowance indicated is included in the estimated costs to cover the undefined scope of the project.

Capital costs given in this report are based on a screening study, as indicated by Fig. D-1, based on general design criteria, block flowsheets, approximate material balances, and data on general equipment requirements. These costs have an accuracy range of +30% to -23%, depending on the reliability of the data, and provide an acceptable basis to determine the most cost-effective alternative within the limits of accuracy indicated.

A. THERMAL OXIDIZER CONTROLLING EMISSIONS FROM CYCLOHEXANE OXIDATION MODEL PLANT HIGH-PRESSURE AND LOW-PRESSURE SCRUBBER VENTS

This example is based on the total combined emissions from the high-pressure and low-pressure scrubbers being 30,000 lb/hr (arrived at by averaging data from two producers) and the VOC and CO quantities listed in Table IV-1. The following data are based on the assumption that the VOC is equivalent to cyclohexane and that the inert gas is essentially nitrogen:

Material	Emission Rate (lb/hr)	Molecular Weight	Emission Rate (lb-moles/hr)
VOC (193 + 30.1) X 2.2	490	84	5.8
CO (486 + 111) X 2.2	1,310	28	46.8
Inert gases (by difference)	28,200	29	972.4
Total	30,000		1025

With the molar volume of 1 lb-mole of gas at 0°C and 1 atm being 359 ft^3, then the emission flow = 1025 X 359 X 1/60 = 6133 scfm.

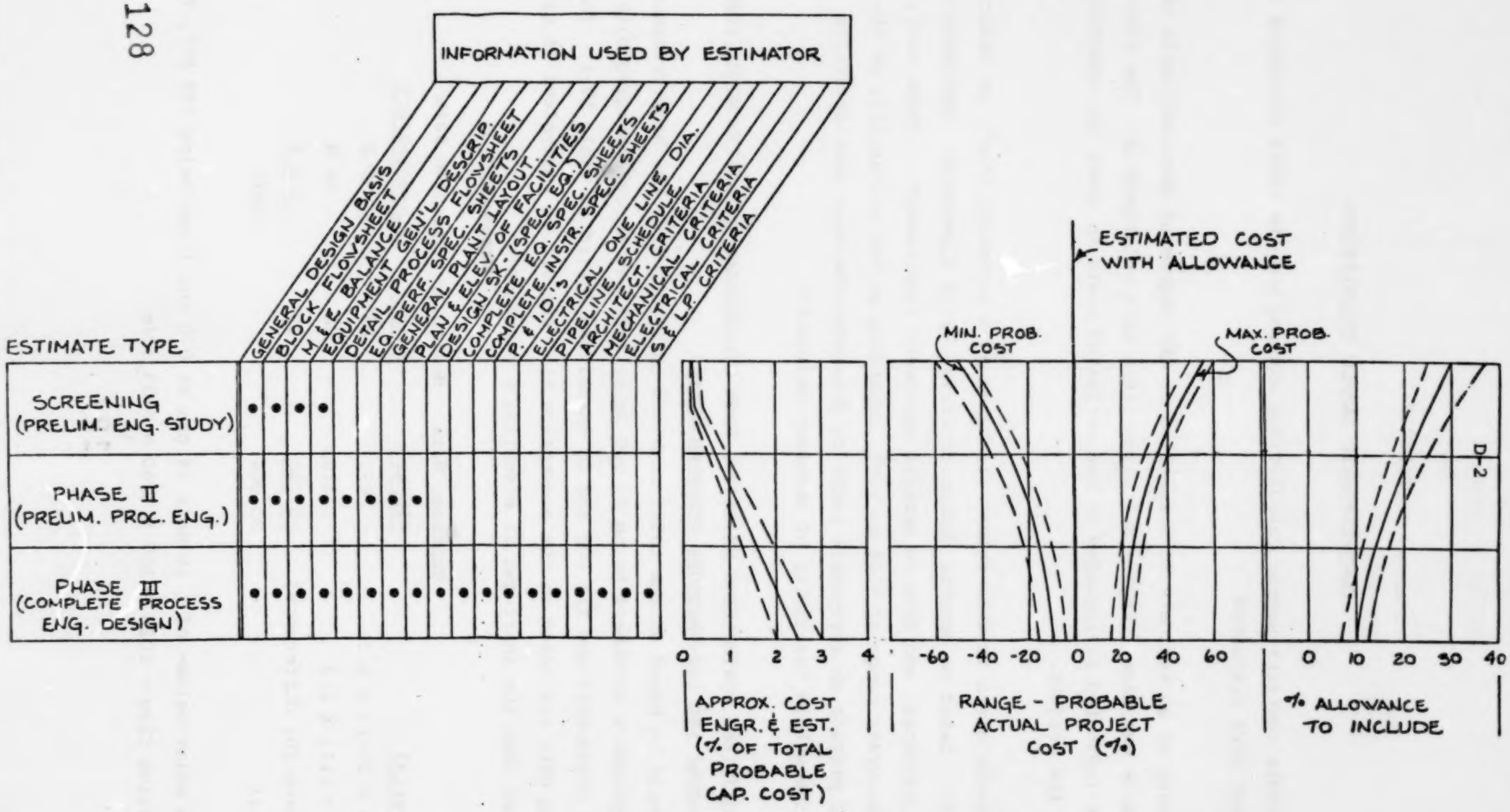


Fig. D-1. Precision of Capital Cost Estimates

LATEST REVISION - 5/2/77

Using the lower heating value of cyclohexane as 18,500 Btu/lb and the heating value of CO as 4,343 Btu/lb, the heating value of emission gases = (490 X 18,500 + 1310 X 4343) X 1/60 X 1/6133 = 40 Btu/scf.

The oxidizer operating conditions are 1600°F at 0.75-sec residence time (Sect. V-A-1 of this report) with 400-psig steam waste-heat boilers. The costs for this system were obtained from Appendix B of the Control Device Evaluation. Thermal Oxidation report.[1] On pages B-20 and B-22 are costs for thermal oxidizers operating at 1600°F and 0.75-sec residence time with feed gas heat contents of 20 and 50 Btu/scf, respectively. Since the costs given in the report do not coincide with the emission conditions of 6133 scfm and 40 Btu/scf, it was necessary to interpolate between the values given by plotting the appropriate values for the 400-psig steam waste-heat boiler case. The following values were obtained:

Total installed capital cost	$800,000
Fixed costs	232,000
Utilities costs	320,000
Manpower costs	36,000
Gross annual operating cost	$588,000
Credit for steam	(334,000)
Net annual operating cost	$254,000

From Table VI-1 of this report the reduction of VOC emissions from the high-pressure and low-pressure scrubbers is 1.93 Gg/yr (1930 Mg/yr); the cost effectiveness is then $254{,}000 \times \frac{1}{1930} = 132$ \$/Mg of VOC.

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[1] J. W. Blackburn, IT Enviroscience, Inc., Control Device Evaluation. Thermal Oxidation (July 1980) (EPA/ESED report, Research Triangle Park, NC).

APPENDIX E

EXISTING PLANT CONSIDERATIONS

A. PROCESS CONTROL DEVICES

Reported controls used by industry are the following:

1. Du Pont Co. at one of their two cyclohexane oxidation process plants has piped the high-pressure scrubber emission off-gas to a plant boiler for incineration.[1]

2. Nipro, Co. at their Augusta, GA, cyclohexane oxidation process facilities uses a flare to control the emissions from the absorbers.[2]

3. Union Carbide Corp. at their Taft, LA, phenol hydrogenation process facilities sends the off-gas after the hydrogenation and dehydrogenation steps to boilers.[3]

B. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

C. REFERENCES*

1. W. R. Chalkers, E. I. du Pont de Nemours & Co., Inc., letter to EPA with information on cyclohexanol/cyclohexanone process, March 12, 1979.
2. W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Nipro, Inc., Augusta, GA, Apr. 18, 1978 (on file at EPA, ESED, Research Triangle Park, NC).
3. F. D. Bess, Union Carbide Corporation, letter to EPA with information on cyclohexanol/cyclohexanone process, May 5, 1978.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 3

CHLOROBENZENES

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Office of Air Quality and Standards
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Research Triangle Park, North Carolina

September 1980

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^1
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^2
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^4
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^1
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^9	1 Gg = 1 X 10^9 grams
M	mega	10^6	1 Mg = 1 X 10^6 grams
k	kilo	10^3	1 km = 1 X 10^3 meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. INTRODUCTION

Production of chlorobenzenes was selected for study because preliminary estimates indicated that the manufacturing process emits significant quantities of benzene, a substance that is listed as a hazardous pollutant by the EPA (Federal Register June 8, 1977). The principal chlorobenzene product is monochlorobenzene; however, o-dichlorobenzene and p-dichlorobenzene are co-produced in significant amounts (see Appendix A for pertinent physical properties).

B. CHLOROBENZENE USAGE AND GROWTH

Table II-1 shows monochlorobenzene end products, and the percentage of total consumption. Table II-2 gives usage for dichlorobenzenes. When this report was first prepared in 1978 the consumption growth rate projected for chlorobenzene varied from reference to reference,[2-7] but it appeared that a 2% growth rate through 1982 was a reasonable consensus. It now appears that the growth rate will be essentially zero through 1982.[1]

The present utilization of production capacity for all chlorobenzene products is about 50%.[1,2]

C. DOMESTIC PRODUCERS

In January 1980, there were five domestic producers of chlorobenzenes, listed in Table II-3 at the plant locations shown in Fig. II-1. All the domestic capacity is based on the direct chlorination of benzene, for which cell chlorine (85 to 95% Cl_2) is generally used. some producers have used purified (condensed, distilled, revaporized) chlorine to improve reaction control and to decrease problems in emission control. Since the chlorobenzene capacity already greatly exceeds the demand, no new plant expansions are anticipated.[2]

D. PRODUCING COMPANIES

1. Dow Chemical USA

Dow, with a mono- and dichlorobenzene capacity of 73 Gg/yr, is the largest producer of these products. Dow also has unlisted production capacities for tri- and tetrachlorobenzene. The tetrachlorobenzene is consumed captively in the manufacture of 2,4,5-TCP herbicide.[2]

Table II-1. Monochlorobenzene Usage (1978)*

End Use	Percent of Consumption
Solvents	42
Nitrochlorobenzene (agricultural (products)	29
DDT, silicones, etc.	8
Diphenyl oxide	11
Rubber intermediates	10

*See ref 1.

Table II-2. Dichlorobenzenes Usage (1978)

End Use	Percent of Consumption
o-Dichlorobenzene[a]	
3,4-dichloroaniline, etc.	70
TDI[b] process solvent	15
Solvents	8
Dye manufacture	4
Pesticides, etc.	3
p-Dichlorobenzene	
Space deodorant	55
Moth control	35
Other	10

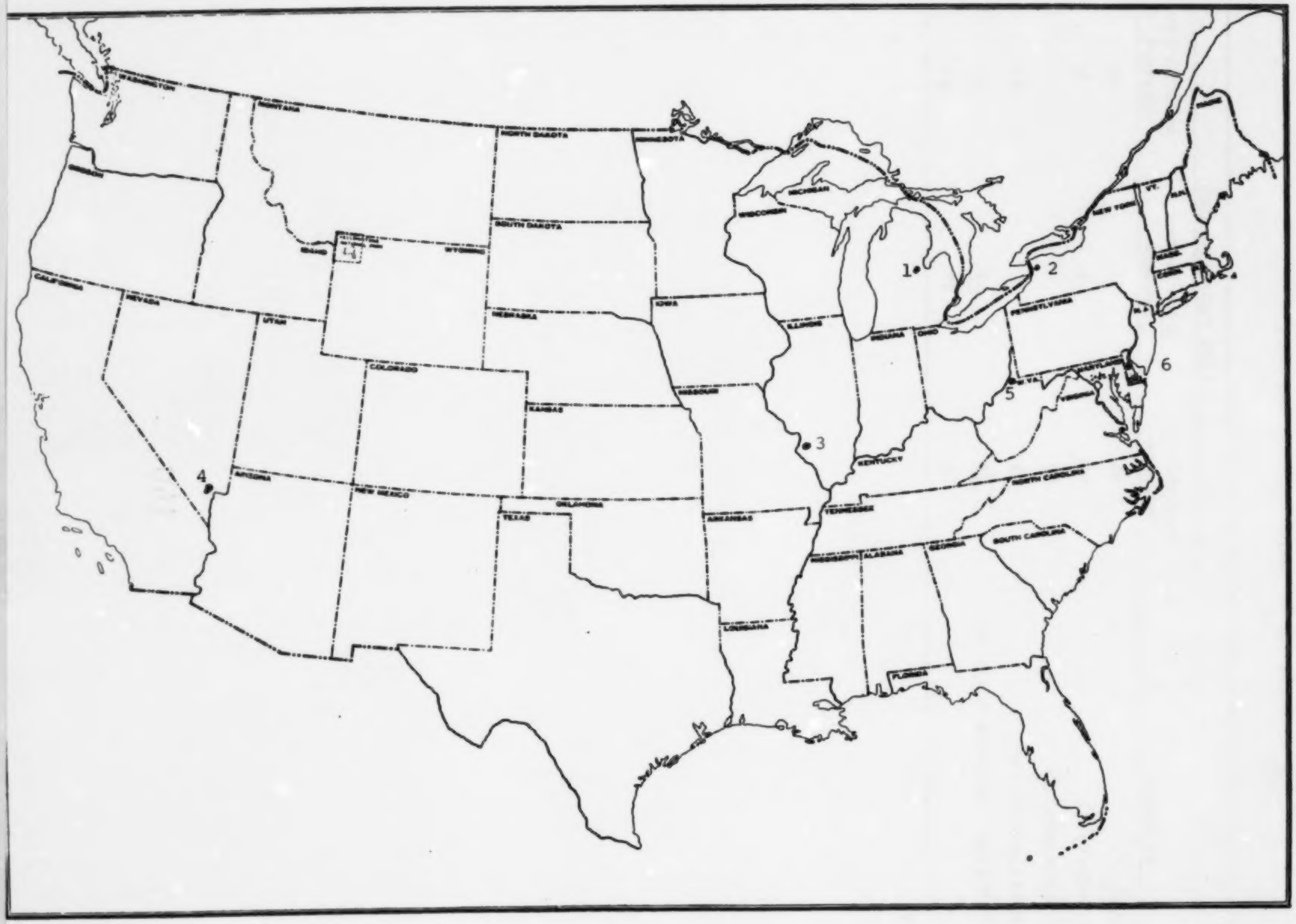
[a] See ref 1.

[b] Toluene diisocyanate.

Table II-3. Chlorobenzene Capacity*

Producer	1980 Capacity (Gg)		
	Monochlorobenzene	o-Dichlorobenzene	p-Dichlorobenzene
Dow, Midland, MI	45	14	14
Monsanto, Sauget, IL	68	3	5
Montrose, Henderson, NV	32		
PPG, New Martinsville, WV	41	9	14
Standard Chlorine, Delaware City, DE	68	23	34
Total	254	49	67

*See ref 1.



1. Dow, Midland, MI
2. ICC, Niagara Falls, NY
3. Monsanto, Sauget, IL
4. Montrose, Henderson, NV
5. PPG, New Martinsville, WV
6. Standard Chlorine, Delaware City, DE

Fig. II-1. Locations of Plants Manufacturing Chlorobenzenes

2. ICC Industries, Inc.

Solvent Chemical Company, a subsidiary of ICC Industries, Inc., ceased operation of it's 11-Gg/yr mono- and dichlorobenzene plant at Niagara Falls, New York in July 1978.[8]

3. Monsanto Company

Monsanto has a mono- and dichlorobenzene capacity of 76 Gg/yr, making it a major producer. Much of the monochlorobenzene is used captively in the manufacture of nitrochlorobenzenes.

4. Montrose Chemical Corporation

All the monochlorobenzene from the Montrose 32-Gg/yr plant is used captively to produce DDT.[2]

5. PPG Industries, Inc.

Expansion of the PPG 64-Gg/yr mono- and dichlorobenzene facility to 113 Gg/yr has been considered but may have been postponed.

6. Standard Chlorine Chemical Co., Inc.

Standard Chlorine is a major producer of mono- and dichlorobenzenes. Their previously listed[1] capacity of 125 Gg/yr was expanded in 1976 but the additional equipment was not started up because of lack of sales growth.[8] Their listed dichlorobenzene capacity is the largest among the producers. They also have unlisted production capacities for tri- and tetrachlorobenzene.

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3. "Chemical Profile on o-Dichlorobenzene," p 9 in Chemical Marketing Reporter, (Sept. 6, 1976).
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8. Letter dated Feb. 5, 1979, to Leslie Evans, EPA, from D. L. Rankin, Dover Chemical Corp.,

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

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III. PROCESS DESCRIPTION

A. INTRODUCTION

Processes for the manufacture of chlorobenzenes have developed over a long period of time, with various chemistry and product separation methods being used.[1] The process currently used by industry is direct chlorination of benzene in the presence of $FeCl_3$ catalyst to produce monochlorobenzene (MCB), according to reaction I in Fig. III-1. The monochlorobenzene reacts with the remaining chlorine to form dichlorobenzenes (DCB), according to reaction 2. Hydrogen chloride is a by-product in both reactions. Only the two major isomers of dichlorobenzene, ortho and para, are shown; however, a very small amount of the meta-isomer is also formed. As chlorination is continued beyond reaction 2, tri-, tetra-, penta-, and, finally, hexachlorobenzenes are formed. Usually, trichlorobenzene is the only one of the more highly chlorinated products found in significant amounts. The degree of chlorination of benzene can be controlled by the choice of catalyst, temperature, and benzene:chlorine ratio in the reactor feed. However, it is not economically possible to exclude the formation of dichlorobenzenes. Therefore, a three-product process is operated to produce monochlorobenzene and o- and p-dichlorobenzenes simultaneously.[1] Hydrogen chloride, a by-product of the reaction, is processed under anhydrous conditions[2] before it is absorbed in water. The reaction and the recovery operations are continuous.[3--5]

B. MODEL PROCESS FOR MANUFACTURE OF CHLOROBENZENE COMPOUNDS

The model* continuous process for the manufacture of chlorobenzenes by chlorination of benzene and separation of the gaseous and liquid products to recover monochlorobenzene and o- and p-dichlorobenzenes is shown in Fig. III-2, Sheet 1. Batch crystallization, solid-liquid separation, freezing, crushing, and screening used in the production of p-dichlorobenzene are shown on Sheet 2.

Most of the steps for the manufacture of monochlorobenzene are generally known in the industry; however, the manner in which some of these steps are carried out varies from company to company and some of the steps, such as the removal of catalyst and the exclusion of water, are subjects of proprietary information. Since corrosion rates can be exceedingly high, violation of the anhydrous conditions can be devastating to operations. These steps are represented in

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*See page I-2 for a discussion of model plants.

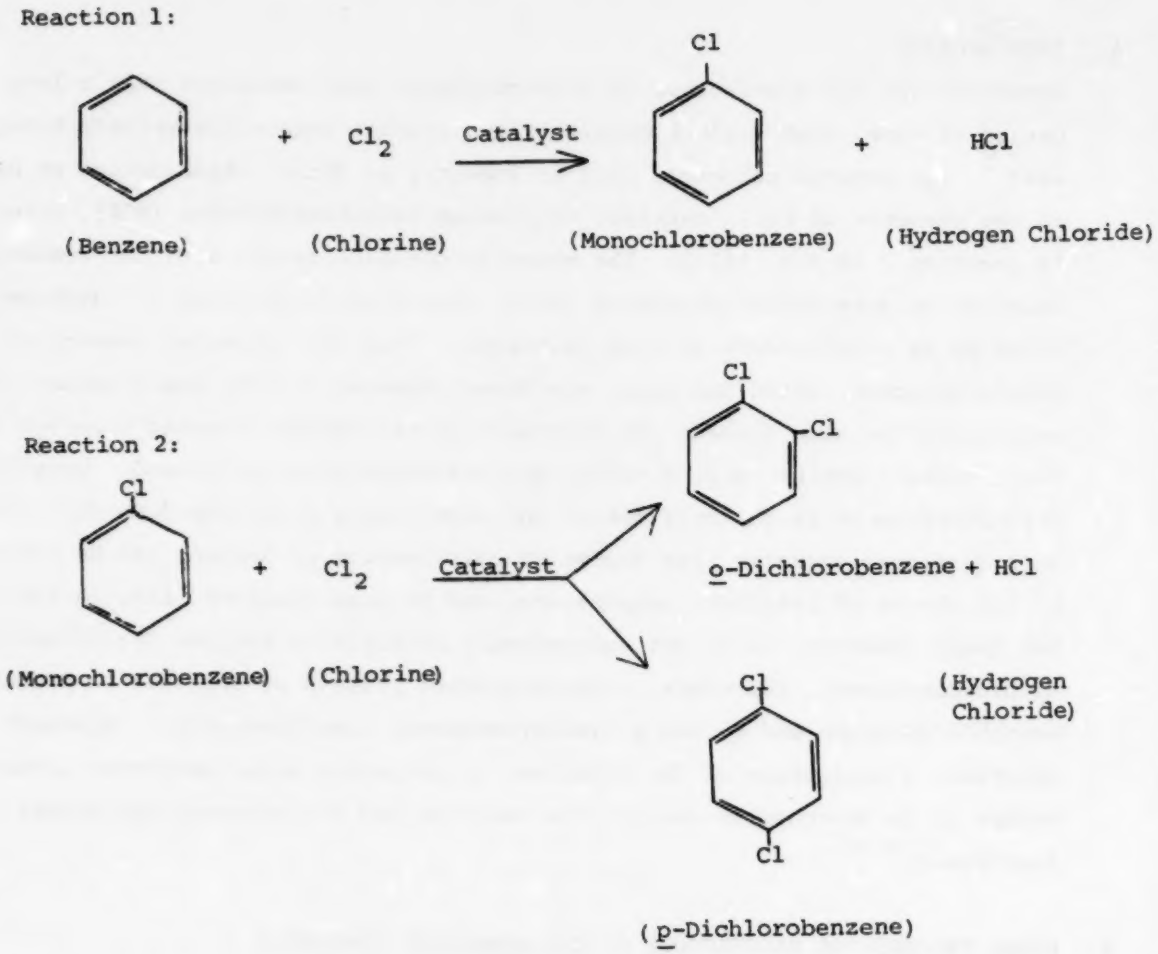

Reaction 1:
Cl
+
Cl2
Catalyst
+
HCl
(Benzene)
(Chlorine)
(Monochlorobenzene)
(Hydrogen Chloride)
Reaction 2:
Cl
+
Cl2
Catalyst
Cl
Cl
o-Dichlorobenzene + HCl
(Monochlorobenzene)
(Chlorine)
Cl
(Hydrogen Chloride)
Cl
(p-Dichlorobenzene)

Fig. III-1. Reactions of Chlorine with Benzene and Monochlorobenzene

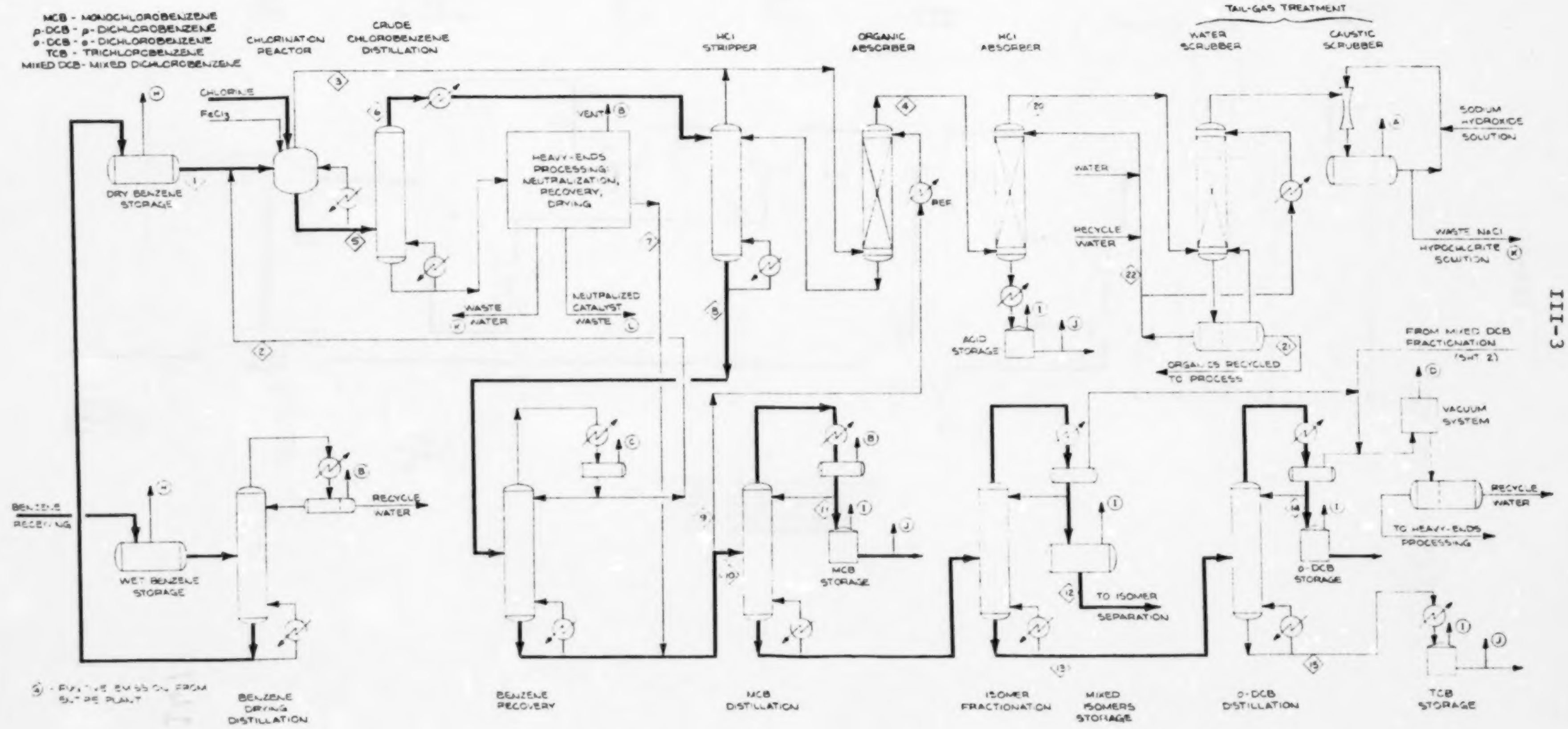
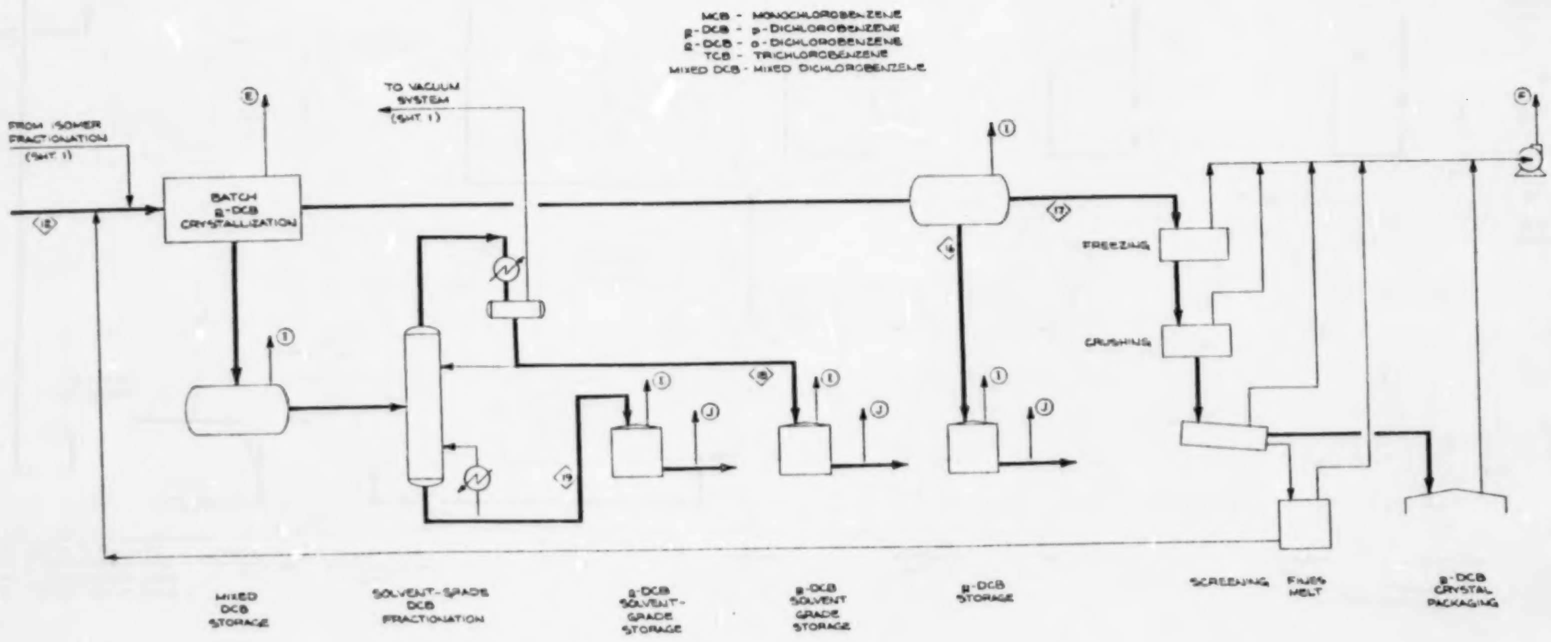

MCB - MONOCHLOROBENZENE
p-DCB - p-DICHLOROBENZENE
o-DCB - o-DICHLOROBENZENE
TCB - TRICHLOROBENZENE
MIXED DCB - MIXED DICHLOROBENZENE
CHLORINATION REACTOR
CRUDE CHLOROBENZENE DISTILLATION
HCl STRIPPER
ORGANIC ABSORBER
HCl ABSORBER
TAIL-GAS TREATMENT
WATER SCRUBBER
CAUSTIC SCRUBBER
CHLORINE
FeCl3
DRY BENZENE STORAGE
HEAVY-ENDS PROCESSING: NEUTRALIZATION, RECOVERY, DRYING
VENT
WASTE WATER
NEUTRALIZED CATALYST WASTE
REF
WATER
RECYCLE WATER
SODIUM HYDROXIDE SOLUTION
WASTE NaCl HYPOCHLORITE SOLUTION
ACID STORAGE
ORGANICS RECYCLED TO PROCESS
FROM MIXED DCB FRACTIONATION (SHT 2)
VACUUM SYSTEM
RECYCLE WATER
TO HEAVY-ENDS PROCESSING
BENZENE RECEIVING
WET BENZENE STORAGE
RECYCLE WATER
MCB STORAGE
TO ISOMER SEPARATION
o-DCB STORAGE
ⓘ - FUGITIVE EMISSION FROM SITE PLANT
BENZENE DRYING DISTILLATION
BENZENE RECOVERY
MCB DISTILLATION
ISOMER FRACTIONATION
MIXED ISOMERS STORAGE
o-DCB DISTILLATION
TCB STORAGE
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
20
21
22
A
B
C
D
H
I
J
K
L

Fig. III-2. Process Flow Diagram for Manufacture of Chlorobenzene Products



MCB - MONOCHLOROBENZENE
p-DCB - p-DICHLOROBENZENE
o-DCB - o-DICHLOROBENZENE
TCB - TRICHLOROBENZENE
MIXED DCB - MIXED DICHLOROBENZENE
FROM ISOMER FRACTIONATION (SHT 1)
12
E
BATCH p-DCB CRYSTALLIZATION
TO VACUUM SYSTEM (SHT 1)
1
14
17
18
19
J
FREEZING
CRUSHING
E
MIXED DCB STORAGE
SOLVENT-GRADE DCB FRACTIONATION
o-DCB SOLVENT-GRADE STORAGE
p-DCB SOLVENT GRADE STORAGE
p-DCB STORAGE
SCREENING
FINES MELT
p-DCB CRYSTAL PACKAGING

Fig. III-2. (Continued)

Fig. III-2 as a block entitled "Heavy-Ends Processing." Since there has been very little growth in the industry in over 10 years,[6] some of the processing steps may represent old designs. The o- and p-dichlorobenzene solvent-grade products are not known commercially by those names. However, they symbolize the lower quality products that are or can be used as intermediates or solvents.

1. Chlorination of Benzene

The first step in the continuous process for producing monochlorobenzene and o- and p-dichlorobenzenes (Fig. III-2, Sheet 1) is removal of the water by distillation from as-received benzene. The dried benzene (Stream 1) and dry recycled benzene (Stream 2) plus the chlorine and the $FeCl_3$ catalysts are fed to the chlorination reactor. The reaction temperature is controlled between 30 and 50°C. The higher the temperature, the larger the amount of dichlorobenzenes formed.[1]

Reactions 1 and 2 of Fig. III-1 are exothermic; for example, the energy release for reaction 1, calculated from heats of formation, is 0.69 MJ/kg of benzene.[7,8] This energy is absorbed partly by cooling and partly by vaporization of some of the reaction mixture components.

2. Recovery of Monochlorobenzene (MCB)

The gas stream from the chlorination reactor (Stream 3), which contains predominantly HCl, unreacted chlorine, inert gases from the chlorine feed, and benzene and other VOC, flows to the organic absorber, where most of the benzene and other VOC are removed. The overhead gas stream, which is low in VOC (Stream 4), then goes to HCl absorption. (See "Recovery of By-Product HCl" below.) The bottoms stream, containing some HCl, is sent to the HCl stripper.

The crude liquid reaction product (Stream 5) is sent to the crude chlorobenzene distillation step. The overhead from the distillation (Stream 6) contains most of the chlorobenzenes, most of the unreacted benzene, and small amounts of HCl. The bottoms stream is sent to heavy-ends processing, where the catalyst is neutralized and some remaining products and higher chlorinated by-products are recovered and dried before being returned to the process (Stream 7). The waste catalyst is discharged for land-fill disposal (Stream L), and the aqueous phase (Stream K) is discharged to wastewater treatment. The HCl that is contained in the overheads from crude chlorobenzene distillation (Stream 6) and in the bottoms from organic absorber is recovered in the HCl stripper. The bottoms stream (Stream 8) is then sent to benzene recovery. Part of the benzene-free stream (Stream 9) is returned to the organic absorber, where it is chilled and used to absorb the benzene and other VOC from the HCl stream. The remainder (Stream 10) is sent to MCB distillation, where the MCB product (Stream 11) is taken overhead and then sent to storage.

3. Recovery of Dichlorobenzenes (DCB)

The residue from MCB distillation contains the DCB isomers. These isomers are fractionated by distillation, with the lower boiling p-DCB and some of the o-DCB going into the overhead along with the m-DCB (Stream 12). The balance of the o-DCB remains in the bottoms (Stream 13).

The bottoms stream is sent to o-DCB distillation, where the o-DCB product is recovered as the overhead (Stream 14) and then sent to storage. The by-product trichlorobenzene remains in the bottoms (Stream 15) and is also sent to storage.

The crude p-DCB in the overheads from isomer fractionation (Stream 12) is purified by batch crystallization. Part of the purified p-DCB (Stream 16) is sent to liquid storage, and the rest (Stream 17) is frozen, crushed, screened, and packaged as p-DCB crystals. During the packaging, ambient air comes in contact with the product and causes some sublimation loss. To keep the p-DCB content in the atmosphere below the hygienic standards of permissible exposure (450 mg/m^3 maximum),[9] the packaging is done in close-fitting hoods. The hoods are exhausted at Vent F.

The mother liquor from the p-DCB crystallization, containing p- and o-DCB and essentially all the m-DCB isomer, is sent to DCB solvent-grade fractionation, where the stream is fractionated into p-DCB solvent-grade (Stream 18) and o-DCB solvent-grade (Stream 19), which are sent to storage.

4. Recovery of By-Product HCl

Gases from the organic absorber (Stream 4) go to the HCl absorber, where, by adiabatic absorption, essentially all the HCl is absorbed. The remaining VOC, unreacted chlorine, water vapor released during absorption of HCl, and inert gases go into the overhead (Stream 20) and to tail-gas treatment, where the water vapor is condensed in the water scrubber and the acid gases are neutralized in the caustic scrubber. The inert gases and small amounts of unabsorbed benzene and VOC are vented (Vent A). The organic layer of the liquid stream from the water scrubber is decanted and recycled to benzene drying (Stream 21), and the aqueous layer containing the dissolved VOC is recycled to the HCl absorber (Stream 22). The aqueous salt stream containing some dissolved VOC is sent to aqueous disposal (Stream K).

C. EMISSION SOURCES

The primary emission in the production of monochlorobenzene and o- and p-dichlorobenzenes results from the tail-gas treatment vent (Vent A), where the inert gases originally contained in the chlorine feed are vented. This vent stream also contains some benzene and chlorobenzenes. Normal practice in the industry is not to provide an emission control device on this vent.

Other emissions include those from benzene drying, heavy-ends processing, benzene recovery, and MCB distillation steps; those from the vacuum system (Vent D) that services the three vacuum stills; and those from batch p-dichlorobenzene crystallization (Vent E). There is also a discharge from the exhaust fan of the hoods in the p-dichlorobenzene crystal-processing area (Vent F), where normally there is no emission control device.

Fugitive emissions occur when leaks develop in valves, pump seals, and major equipment (Discharge G). In a process that is as potentially corrosive as the chlorination of benzene a water leak into the system that contains HCl can rapidly create leaks that will significantly contribute to benzene and VOC losses to the environment. Losses can also occur through seals and moving and vibrating parts of the mechanical equipment used in p-dichlorobenzene crystal processing.

Storage emission sources include benzene storage (Vent H) and various chlorobenzene product storages (Vent I), including monochlorobenzene, crude p-dichlorobenzene, mixed dichlorobenzenes, and finished o- and p-dichlorobenzenes.

Handling emissions (Vent J) result from the loading of monochlorobenzene, *o*- and *p*-dichlorobenzene products, and trichlorobenzene.

Secondary emissions can occur when wastewater streams containing dissolved benzene and other VOC (Stream K) are treated in a waste-treatment plant and when the catalyst waste (Stream L) is discharged to a controlled land fill.

D. PROCESS VARIATIONS

The chlorine used to produce mono- and dichlorobenzenes in the model plant is 99% pure, which is the purity being achieved by some of the producers. Chlorine containing up to 15% or more inert gases is used by older plants, which causes the amount of VOC emission from Vent A to be proportionately higher. If the water scrubber has no decanter or if inadequate provision is made for phase separation and the liquid discharges to wastewater treatment, the secondary emission potential will be greatly increased.

A caustic scrubber is not always used following the water scrubber. A caustic scrubber may not significantly affect the VOC in the vent stream; however, it will absorb the traces of HCl and chlorine and reduce the corrosiveness of the vent stream to the surrounding steel equipment.

Variations in the removal of the catalyst and the high-boiling organic residues from the process can affect emission rates. For example, if the material is hot and under a positive pressure when discharged, the benzene and other VOC emissions will be greater.

Freezing, crushing, screening, packaging, or weighing of p-dichlorobenzene crystals, if conducted in open equipment, will result in increased sublimation and loss of the product. Since the vapor concentration in the work area must be maintained below industrial hygiene standards, a large movement of air will be required. This would necessitate larger equipment for emission control. The variations among manufacturers in the processing steps following the recovery of monochlorobenzene can result in differences in emissions. Some manufacturers market a mixed dichlorobenzene product, which requires fewer separation steps.[5] Such a process will have fewer emission points and a lower emission ratio.

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IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. MODEL PLANT

The process emissions estimated for the model plant are based on the emissions reported in response to EPA's request for information from selected companies, on Monsanto and PPG Industries trip reports, on SRI information and an understanding of the process chemistry.

The yearly production capacity of the model plant developed for this study is 68 Gg of monochlorobenzene, 12.4 Gg of o-dichlorobenzene, and 15.6 Gg of p-dichlorobenzene, for a total of 96 Gg of chlorobenzene products and 36 Gg of by-product HCl. One half of the p-dichlorobenzene is estimated to be sold as a crystal product and half as a liquid. The size of the model plant is typical of the larger plants. The process, shown in Fig. III-2, is based on a knowledge of today's chlorobenzene manufacturing industry with the application of current engineering technology of continuous chlorination, separation in a single-train process, and resource recovery. From an emission standpoint the model plant is more representative of the best processes in operation today and of what would be expected from future construction than representative of today's total industry.

Benzene is chlorinated in the presence of $FeCl_3$ catalyst to form the three major products and HCl. Separation steps include distillation for benzene drying, benzene recovery, HCl separation, and product separation; absorption for HCl recovery; crystallization for p-dichlorobenzene purification; and solids processing for production of p-dichlorobenzene crystals.

Process emissions estimated for the model uncontrolled plant are discussed in Sect. IV.B.[1--5] Estimates of potential fugitive-emission sources based on data from existing facilities are discussed in Sect. IV.B.6. Raw-material, intermediate, and product storage-tank capacities were estimated, and their emissions are discussed in Sect. IV.B.7. Estimates of potential emissions from secondary sources are discussed in Sect.IV.B.8. Characteristics of the model plant that are important in air-disperson modeling are shown in Appendix B.

B. SOURCES AND EMISSIONS

The uncontrolled emission rates from all sources for the chlorobenzene process are summarized in Table IV-1, and the process vent locations are shown in Fig. III-2.

1. Tail-Gas Scrubber

The largest process emission of benzene and total VOC is from tail-gas treatment (Vent A), which is the reactor vent for inert gas.[1--3] The emissions from this vent are directly related to the inert-gas content of the chlorine feed and to the production rate. The chlorine feed for the model plant is considered to be 99 vol % chlorine, the balance being inert gases. At capacity operation the VOC emission is estimated to be 6.7 kg/hr, of which 5.7 kg/hr is benzene.

During startup the venting would be somewhat higher because the inert gases trapped in the system would have to be purged.

2. Atmospheric Distillation Vents

The dissolved gases and the uncondensed VOC from benzene drying, benzene recovery, heavy-ends processing, and monochlorobenzene distillation sections are emitted from these vents (Vents B,C). The quantities are, to a large extent, related to production. The VOC emission rate is estimated to be 4.3 kg/hr, of which 4.0 kg/hr is benzene.

3. Vacuum System Vent

The air that leaks into the isomer fractionation, o-dichlorobenzene distillation, and solvent-grade dichlorobenzene fractionation columns is discharged from the vacuum system at Vent D. This discharge carries with it uncondensed VOC.

Table IV-1. Benzene and Total VOC Uncontrolled Emissions from Model Plant for Chlorobenzene Products

Source	Stream Designation (Fig. III-2)	Emission Ratio (g/kg)*		Emission Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC
Tail-gas scrubber treatment	A	0.52	0.61	5.7	6.7
Atmospheric distillation vents	B	0.32	0.35	3.5	3.8
Atmospheric distillation vent	C	0.04	0.04	0.48	0.48
Vacuum system vent	D		0.46		5.1
p-DCB crystallization vent	E		0.016		0.18
p-DCB crystal processing vent	F		0.084		0.92
Fugitive	G	0.58	1.97	6.4	21.6
Benzene storage	H	0.41	0.41	4.5	4.5
Other storage			0.14		1.6
Handling	I,J		0.02		0.23
Secondary	K,L	0.019	0.030	0.21	0.33

*g of benzene or total VOC per kg of chlorobenzene products.

The emission from this vent is essentially fixed for a given plant design and does not vary significantly with the throughput rate.

4. p-Dichlorobenzene Crystallization

The venting from the crude p-dichlorobenzene crystallization section (Vent E) represents the displacement loss in batch processing. The vent lines of the equipment in this section are interconnected to prevent further displacement losses.

5. p-Dichlorobenzene Crystal Processing

The process emissions from freezing, crushing, and screening operations are not significant. (Fugitive emissions from the equipment, which can be significant, are discussed later.) During packaging and weighing of the finished crystals a sweep of air is drawn across the exposed crystals by an exhaust fan in order to maintain the p-dichlorobenzene content of the air in the work area to less than 450 mg/m^3, which is the accepted standard for this material.[4] The loss during p-DCB crystal processing results in a VOC emission of 0.92 kg/hr. The emissions are directly related to throughput and are seasonal, higher during the summer and lower during the winter.

6. Fugitive Emissions

Process pumps and valves are potential sources of fugitive emissions (Vent G). The model plant is estimated to have 102 pumps handling VOC, 22 of which handle benzene, 68 handle other light liquids and 12 handle heavy liquids. The estimated number of valves is 792, 45 of which service benzene vapor, 61 service other VOC vapor, 173 service benzene liquid, 421 service other light liquids and 92 service heavy liquids. The estimated number of pressure relief valves is 12, 6 of which wervice benzene, 5 service other light liquids, and 1 services heavy liquids. The estimated number of flanges is 1848, of which 486 service benzene and 1328 service other VOC. The fugitive emission factors from Appendix C were applied to this valve, pump, and flange count to determine the fugitive emissions shown in Table IV-1. Significant fugitive emissions can occur if freezing, crushing, or screening operations are conducted in open equipment or if there are loose-fitting flexible joints between pieces of equipment. Data were not obtained to estimate losses from these sources.

7. Storage and Handling Emissions

Emissions result from the storage and handling of benzene, monochlorobenzene, p- and o-dichlorobenzenes, trichlorobenzene residues, and in-process streams. Sources of losses for the model plant are shown in Fig. III-2 (sources H, I, and J). Storage tank conditions for the model plant are given in Table IV-2. The storage- and handling-emission calculations in Table IV-1 were based on fixed-roof tanks, half full, and a diurnal temperature variation of 11°C and with the use of the emission equations from AP-42.[5] However, breathing losses were divided by four to account for recent evidence indicating that the AP-42 breathing loss equation overestimates emissions.[6]

Since benzene freezes at 5.5°C, p-dichlorobenzene freezes at 53°C, and trichlorobenzene residues freeze at about 20°C, the storage tanks containing these materials are heated as necessary to maintain their temperatures above the freezing point.

Emissions from barge loading of monochlorobenzene and tank car loading of o- and p-dichlorobenzenes and trichlorobenzene were calculated with the equations from AP-42.[5] VOC emissions from storage and handling are estimated to be 6.3 kg/hr, or which 45 kg/hr is benzene.

8. Secondary Emissions

Secondary emissions of benzene and other VOC can result from the handling and disposal of wastewater streams. For the model plant two potential sources of secondary emissions from wastewater are indicated in Fig. III-2 (Source K): the aqueous purge stream from the caustic scrubber in tail-gas treatment and the aqueous effluent from heavy-ends processing. It is estimated that 50% of the benzene and 25% of the other VOC contained in these streams are emitted.

The neutralized catalyst waste (Source L) contains high-boiling chlorinated benzenes and decomposition products. Incineration of this waste may result in some emission. Disposal in land fill may result in a minor emission. It is estimated that <2% of the organic is emitted during disposal.

Table IV-2. Model Plant Storage Tank Data

Content	Number	Tank Size (m^3)	Turnovers per Year	Bulk Liquid Temperature (°C)
Benzene, wet (bulk)	2	1900	19	20
Benzene, wet (working)	2	230	155	20
Benzene, dry (working)	1	230	Constant level	20
Monochlorobenzene (working)	2	230	134	35
Monochlorobenzene (bulk)	3	1900	11	16
HCl solution (bulk)	2	1900	13	16
p-Dichlorobenzene (crude)	2	90	75	75
p-Dichlorobenzene (working)	3	40	98	75
p-Dichlorobenzene (bulk)	1	460	12	75
o-Dichlorobenzene (working)	2	40	102	35
o-Dichlorobenzene (bulk)	1	830	10	16
Mixed dichlorobenzene (working)	1	40	51	35
o-DCB solvent grade (bulk)	2	60	11	16
p-DCB solvent grade (bulk)	2	40	9	75
Trichlorobenzene (bulk)	2	40	4	50

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6. Letter dated May 30, 1979, from E. C. Pulaski, TRW, Inc., to Richard Burr, EPA.

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V. APPLICABLE CONTROL SYSTEMS

A. TAIL-GAS TREATMENT (VENT A)

The emissions from the caustic scrubber of the tail-gas treatment step can be effectively reduced by a carbon adsorption (CA) system; however, the VOC concentration in Vent A is too high for efficient control by carbon adsorption. Dilution with a carrier gas, which is provided by the combination of this stream with other emissions as described later is this report, is necessary for efficient control. The vent gas from the caustic scrubber, being essentially saturated with water, is heated to reduce the relative humidity. Since chlorobenzene products have a slight tendency to hydrolyze under the conditions of operation, the material of construction must be capable of withstanding the resulting corrosive environment. The process equipment must have safeguards to ensure that malfunction or misoperation of the caustic scrubber system does not allow free chlorine to pass into the CA system where it could cause a reaction leading to fire or explosion.

After the vent gas from the tail-gas treatment has been conditioned, it passes through one of the adsorber beds. The VOC-depleted gas is then released to the atmosphere. When the first bed approaches breakthrough, the conditioned feed gas is routed to the second bed. At this time regeneration of the first bed by steam stripping is started. The VOC-laden effluent vapor is then condensed and decanted. The organic layer is recycled to the process, and the VOC-saturated aqueous layer is recycled to HCl absorption. When essentially all the VOC are stripped from the first bed, air supplied by a purge-gas fan is sent through the first bed to cool it and make it ready for adsorption. The purge gas discharged is sent to the adsorbing bed for removal of the small amount of VOC that it contains. A removal efficiency of 98.7%* is considered to be attainable under the above conditions,[1] and has been used to project the final emissions from the model controlled plant (Table V-1). The net annual cost of this system is shown in Table VI-2 of Sect. VI.

B. ATMOSPHERIC DISTILLATION VENTS

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*Based on a carbon adsorption effluent concentration of 12 ppm_v VOC.

Table V-1. Benzene and Total VOC Controlled Emissions from Model Plant for Chlorobenzene Products

Source	Stream Designation (Fig. III-2)	Control Device or Technique	Emission Reduction (%)	Emission Ratio (g/kg)*		Emission Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
Tail gas treatment	A	Carbon adsorption	98.7	0.0067	0.0079	0.074	0.087
Atmospheric distillation vents	B	Carbon adsorption	98.7	0.0042	0.0045	0.045	0.049
Atmospheric distillation vents	C	Vent to process	100				
Vacuum system vent	D	Carbon adsorption	98.7		0.006		0.066
p-DCB crystallization vent	E	None			0.016		0.18
p-DCB crystal processing vent	F	Carbon adsorption	98.7		0.001		0.012
Fugitive	G	Detection and repair of major leaks	71	0.16	0.58	1.77	6.17
Benzene storage	H	Internal floating roof	85	0.06	0.06	0.67	0.67
Other storage and handling	I,J	None			0.16		1.83
Secondary	K,L	None		0.019	0.030	0.21	0.33

---

* g of benzene or total VOC per kg of chlorobenzene products.

1. Benzene Drying (Vent B)

The emission from benzene drying is a small portion of the total emissions from the process and can be combined with other emissions to be sent to the carbon adsorber system for control. A removal efficiency of 98.7% is estimated to be attainable for this stream.

2. Heavy-Ends Processing (Vent B)

The quantity of emissions from the process step is small but it may contain benzene and may be subject to process upsets. If this stream is brought in contact with caustic in heavy-ends processing, additional conditioning will not be necessary before it is sent to the carbon adsorption system.

3. Benzene Recovery (Vent C)

The discharge from benzene recovery is estimated to contain a small quantity of HCl remaining from the HCl stripping step. This discharge is compatible with and connected to the gas stream going to the organic scrubber in the model controlled plant. Any inert gas present is eventually processed through the carbon adsorption system.

4. MCB Distillation (Vent B)

The discharge from MCB distillation contains a small amount of inert gas and any benzene remaining from the benzene recovery step. This discharge can be combined with other streams that feed the carbon adsorption system without the need for additional conditioning. A removal efficiency of 98.7% is considered to be attainable for this stream.

C. VACUUM SYSTEM VENTS (VENT D)

The discharge from the vacuum system vent contains benzene, other VOC, and air that has leaked into the three vacuum distillation volumns. This stream is estimated to be slightly acidic and requires materials of construction capable of withstanding the environment. This discharge can be combined with other streams that feed the carbon adsorption system with no additional conditioning. Again, the removal efficiency for this stream is considered to be 98.7%.

D. p-DCB CRYSTALLIZATION (VENT E)

The discharge from the p-DCB crystallization represents displacement loss due to batch processing and is relatively low in significance; therefore control is not considered necessary.

E. p-DCB CRYSTAL PROCESSING (VENT F)

The discharge from p-DCB crystal processing results from air movement in the crystal packaging area that is needed to maintain compliance with industrial hygiene standards regarding p-DCB concentration in the work environment.[2] This discharge is incorporated with the other feeds to the carbon adsorption system and provides the dilution needed for efficient adsorption and control of VOC. The removal efficiency here is also estimated to be 98.7%.

F. FUGITIVE SOURCES (DISCHARGE G)

Control for fugitive sources is discussed in a separate report covering fugitive emissions from the synthetic organic chemicals manufacturing industry (SOCMI). The controlled fugitive emissions shown in Table V-1 were calculated with the factors given in Appendix C. These factors are based on the assumption that any major leaks will be detected and repaired.

G. STORAGE AND HANDLING SOURCES

1. Benzene Storage (Vent H)

Control of benzene storage emissions from the SOCMI is discussed in a separate EPA report. A floating roof is commonly used on storage tanks to control emissions from chemicals in the vapor pressure range of benzene. The internal-floating-roof tanks* used in the model controlled plant are assumed to reduce the fixed-roof-tank emissions by 85%.[3]

2. Other Storage and Handling (Vents I and J)

The storage of nonbenzene VOC results in a calculated average emission of 2.97 kg/hr from 23 storage tanks. The largest single emissions is 0.42 kg/hr. This single nonbenzene VOC emission is not considered to be sufficiently large to warrant control. The calculated losses[3] during loading of products into barges and tank cars result in an average VOC emission of 0.23 kg/hr.

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*Consist of internal floating covers or covered floating roofs as defined in API 25-19, 2d ed., 1976 (fixed roof tanks with internal floating device to reduce vapor loss).

H. SECONDARY SOURCES (DISCHARGES K AND L)

Secondary emissions can result from handling and treating the wastewater (Discharge K) in typical wastewater treatment facilities. This emission may be reduced by steam stripping the wastewater and recycling the benzene and other VOC but no provision has been made in the model controlled plant for this control method. It is assumed that the periodic disposal of spent carbon will be by land-fill or equivalent and that VOC will be removed as much as possible by steaming prior to disposal. The control of secondary emissions is further discussed in a separate EPA report. No alternate system to incineration or land-filling operation has been identified for the waste catalyst (Discharge L).

I. CURRENT EMISSION CONTROL

The information available concerning the emissions and emission controls currently used by existing chlorobenzene producers in the United States is presented in Appendix D.

REFERENCES*

1. H. S. Basdekis, IT Enviroscience, Control Device Evaluation - Carbon Adsorption (in preparation for EPA, ESED, Research Triangle Park, NC.)

2. D. D. Irish, "Halogenated Hydrocarbons: II. Cyclic," pp 1337--1340 in Industrial Hygiene and Toxicology, edited by F. A. Patty *et al.*, vol. II, 2d ed., Interscience, New York, 1963.

3. Letter dated Aug. 15, 1979, from W. T. Moody, TRW, Inc., to David Beck, EPA.

4. C. C. Masser, "Storage of Petroleum Liquids," pp 4.3-12 and 4.3-13 in Supplement No. 7 for Compilation of Air Pollutant Emission Factors, AP-42, 2d ed., EPA, Research Triangle Park, NC (April 1977).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. CONTROL COST IMPACT

This section presents estimated costs and cost-effectiveness data for control of benzene and total VOC process emissions by use of a carbon adsorption emission control system. Details of the model plant (Fig. III-2) are given in Sects. III and IV. The capital and annual costs presented for the process emission controls were obtained from the Control Device Evaluation Report for Carbon Adsorption (CA).[1] The procedure used to develop the costs for this control system is detailed in Appendix E.

Capital cost estimates represent the total investment required to purchase and install all equipment and material required to provide a complete process emission control system performing as defined for a new plant at a typical location. These estimates do not include the cost of production lost during installation or startup, of research and development, or of land acquisition. The capital costs do not include the cost of safeguards in the process to ensure that malfunction or misoperation of the caustic scrubber system does not allow free chlorine to enter the CA system where it could cause a reaction leading to fire or explosion. The costs also do not include incorporation of a device, such as an induced draft fan, that may be desired to protect against possible backflow into one of the 6 process waste gas vents joined together to feed the carbon adsorption system. These items are considered highly site specific.

The bases for the annual cost estimates for the carbon adsorption (CA) control system includes utilities, operating labor, maintenance supplies and labor, capital recovery charges, chemical recovery credits, and miscellaneous recurring costs such as taxes, insurance and administrative overhead. Chemicals recovered are taken as raw material value. Chlorobenzene recovered is credited with the benzene and chlorine equivalent. Annual costs are for a 1-year period beginning in December 1979. Cost and design factors used are itemized in Table VI-1.

Process Emissions A, B, D, and F

These streams vent the discharges from tail-gas treatment, benzene drying, heavy-ends processing, monochlorobenzene distillation, vacuum system, and p-DCB

Table VI-1. Cost and Design Factors to Carbon Adsorption Emission Control System

3 hr loading cycle	
Carbon loading	6 kg VOC/100 kg carbon
Steam for regeneration	1 kg/kg of carbon
Steam for gas conditioning	35.2 kg/hr
Gas velocity	30.5 meters/min (100 ft/min)
Bed depth	0.9 meters (3 ft)
Pressure drop	5,257 pascals/meter (6.5 in H_2O/ft)
Carbon	4 X 10 mesh BPL carbon 480 kg/m^3 (30 lb/ft^3)
Benzene equivalent recovery credit	$0.22/kg ($0.10/lb)
Chlorine equivalent recovery credit	$0.15/kg ($0.07/lb)
CA minimum effluent concentration	12 ppm$_v$ VOC
Granular activated carbon replacement every 5 yrs	($1.17/lb)[a]
Operating factor	8760 hr/yr[b]
Steam cost	$5.50/Mg ($2.50/M̄ Btu)
Electric power	$8.33/GJ ($0.03/kWh)
Fixed cost	
Maintenance labor plus materials, 6% Capital recovery, 18%[c] Taxes, insurance, administration charges, 5%	29% installed capital

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[a] If it became necessary to replace the carbon every 2 yrs, the annual cost would increase 1.4% ($1,270/yr).

[b] Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

[c] Based on 10-year life and 12% interest.

crystal processing. The estimated installed capital cost of a carbon adsorption system to reduce total VOC emissions, including benzene, from the model chlorobenzene products plant is $325,000 (see Appendix E). This cost is based on the installation of a 2-bed, carbon adsorption system, which includes blowers, condenser, decanter, interconnecting piping, valving, instrumentation, and all necessary duct work and utility connections for a complete installation. Since the vent gas rate varies directly with production, a plant twice the size of the model plant would have twice the emissions from these vents. Figure VI-1 shows the variation of capital cost of a carbon adsorption system with plant capacity.

To determine the cost effectiveness of controlling process emissions by carbon adsorption, the costs obtained from the CA report[1] have been adjusted to include the additional capital and operating expenses for preconditioning the process waste gas and the need for costly equipment linings because of the corrosiveness of the waste gas. The results of the cost adjustment and emission reduction cost effectiveness calculation are as follows:

Annual cost from CA report[10] Fig. IV-4	$80,416
Fixed cost adjustment	36,250
R.M. credit	(30,618)
Steam for conditioning	1,686
Net annual cost	$87,734

Benzene emission reduction	79.5 Mg/yr
Total VOC emission reduction	143 Mg/yr
Cost effectiveness	
Cost per Mg of benzene emission reduced	$1104
Cost per Mg of total VOC reduced	$613

The details for estimating the costs and cost effectiveness for the control of emissions from chlorobenzene plants ranging in size from 50% of the model plant capacity to a capacity 50% greater than the model plant are given in Appendix E. The results are plotted on Figs. VI-1, VI-2, and VI-3.

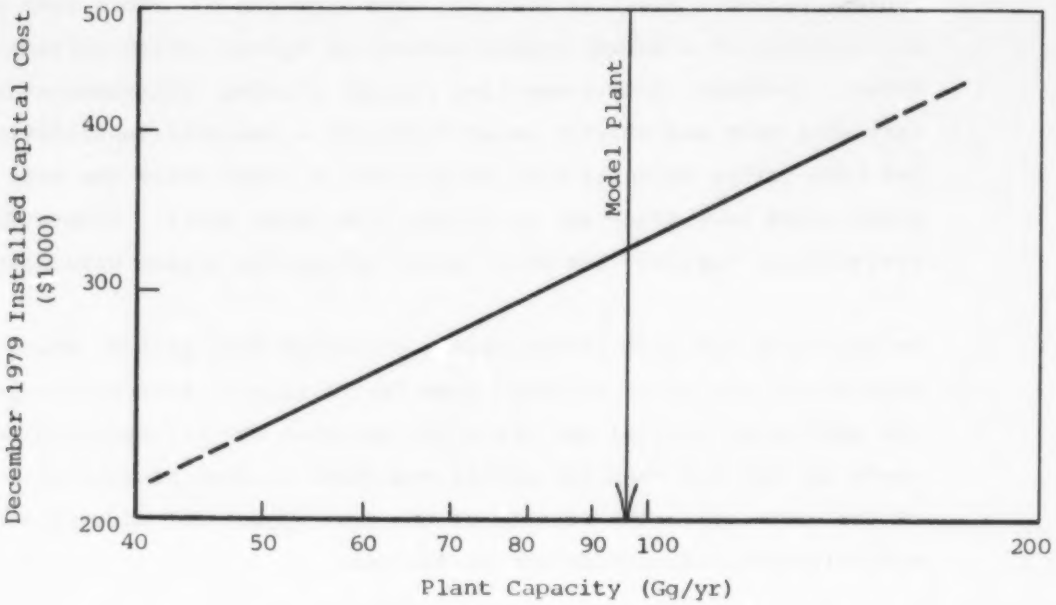

Fig. VI-1. Installed Capital Cost vs Plant Capacity for Carbon Adsorption Emission Control System

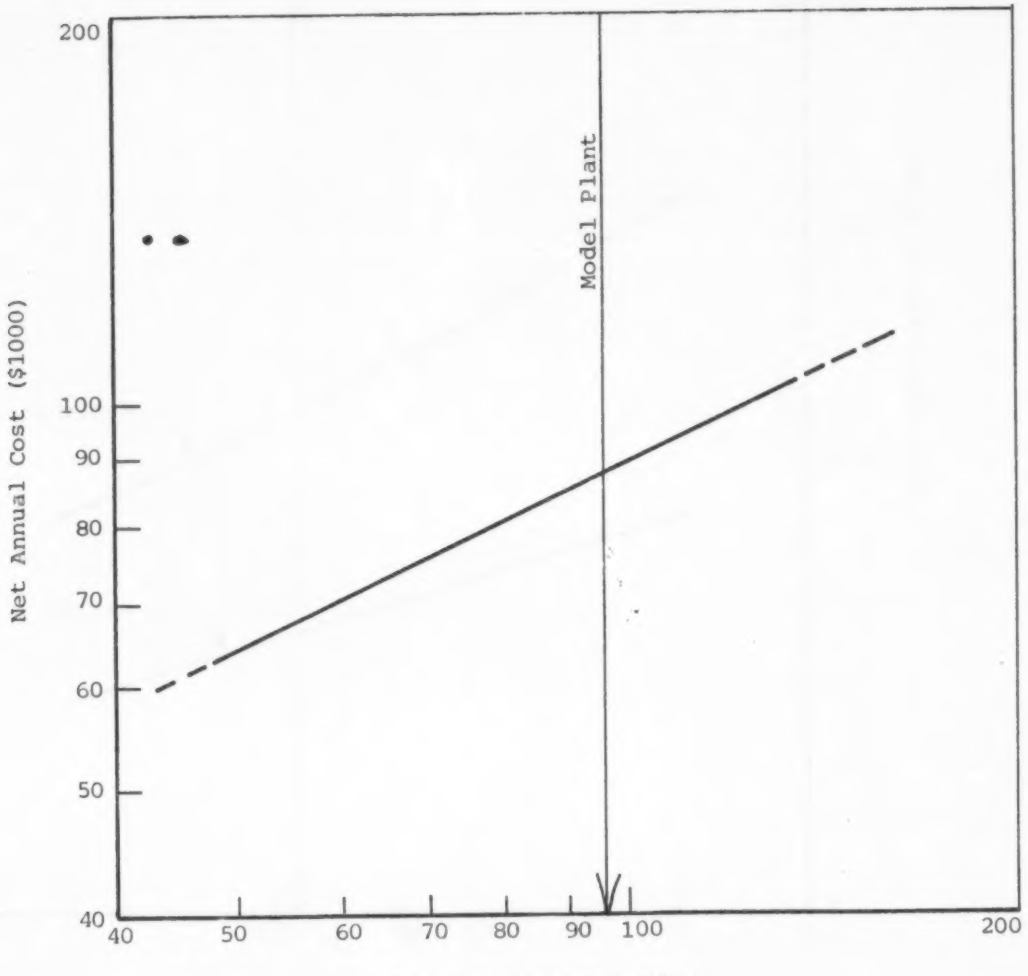

Fig. VI-2. Net Annual Cost vs Plant Capacity for Carbon Adsorption Emission Control System

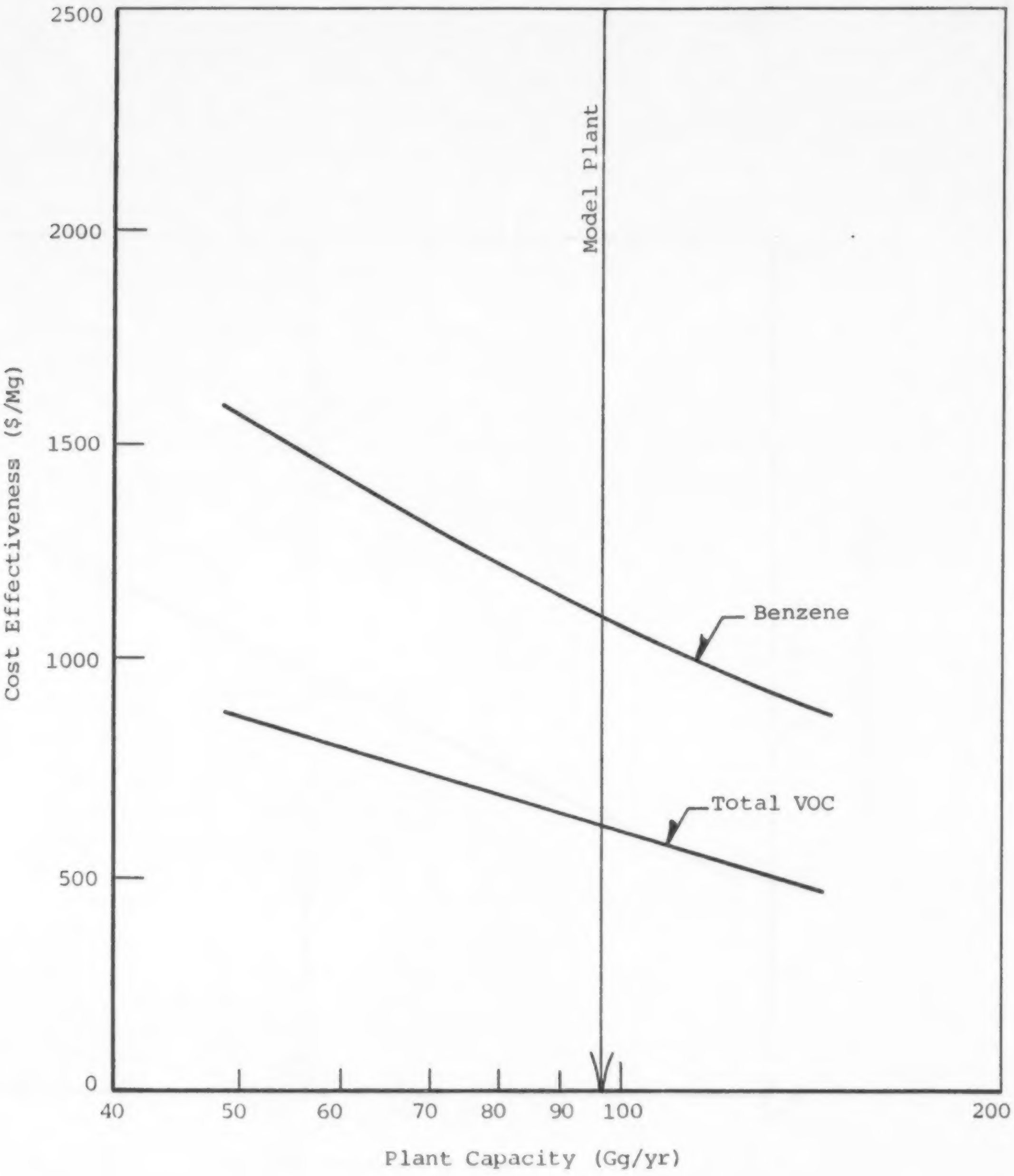

Fig. VI-3. Cost Effectiveness vs Plant Capacity for Carbon Adsorption Emission Control System

2. Benzene Storage

Model-plant benzene storage emissions are controlled by the use of internal floating-roof tanks. Installed capital cost, net annual cost, and cost-effectiveness data for retrofitting the model plant fixed-roof tanks and for the incremental costs of new internal-floating-roof tanks (based on the capital cost of new internal-floating-roof tanks minus capital cost of new fixed- roof tanks) are given in a separate EPA report.[2]

3. Fugitive Sources

Control emission factors for fugitive sources are described in Appendix C. A separate EPA report will cover fugitive emissions and their applicable controls for the synthetic organic chemicals manufacturing industry.[3]

4. Secondary Sources

No control system has been defined for secondary emissions from the model plant. Secondary sources and their control are discussed in a separate EPA report.[4]

B. ENVIRONMENTAL AND ENERGY IMPACTS

Table VI-2 shows the environmental impact of reducing benzene and total VOC emissions by the application of the described control systems for the model plant.

1. Carbon Adsorption System

This system is designed for the model plant to reduce the benzene emissions by 79 Mg/yr and total VOC emissions by 143 Mg/yr. Operation of this unit consumes steam at the rate of 7122 GJ/yr including conditioning and electric power for pumps at the rate of 522 GJ/yr.

2. Floating-Roof Storage

The use of floating-roof tanks for control of benzene emission from storage does not consume energy and has no adverse environmental or energy impact.

Table VI-2. Environmental Impact of Controlled Model Plant

Source	Steam Designation (Fig. III-2)	Control Device or Technique	Emission Reduction (%)	Emission Reduction (Mg/yr)	
				Benzene	Total VOC
Tail-gas treatment	A	Carbon adsorption	98.7	49	58
Atmospheric distillation vents	B	Carbon adsorption	98.7	30	33
Atmospheric distillation vent	C	Vent to process	100	4.1	4.1
Vacuum system vent	D	Carbon adsorption	98.7		44
p-DCB crystallization vent	E	None			
p-DCB crystal processing vent	F	Carbon adsorption	98.7		8.0
Fugitive	G	Detection and repair of major leaks	71	40	130
Benzene storage	H	Internal floating roof	85	33	33
Other storage and handling	I,J	None			
Secondary	K,L	None			
				156	310

REFERENCES*

1. H. S. Basdekis, IT Enviroscience, Control Device Evaluation - Carbon Adsorption (in preparation for EPA, ESED, Research Triangle Park, NC).
2. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling Report, (in preparation for EPA, ESED, Research Triangle Park, NC).
3. D. G. Erikson, IT Enviroscience, Inc., Fugitive Emission Report, (in preparation for EPA, ESED, Research Triangle Park, NC).
4. J. J. Cudahy, R. L. Standifer, IT Enviroscience, Secondary Emissions Report, EPA, ESED, Research Triangle Park, NC, June 1980.

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VII. SUMMARY

The chlorobenzene products, monochlorobenzene, o-dichlorobenzene, and p-dichlorobenzene, are produced in the United States by $FeCl_3$-catalyzed direct chlorination of benzene, wherein HCl is generated as a by-product.

It is estimated that the present utilization of chlorobenzene products represents about 50% of the current domestic capacity of 370 Gg/yr. Zero growth is projected for chlorobenzene products through 1982. No shortage of benzene is expected during this period.[2]

Emission sources and control levels for the model plant are summarized in Table VII-1. The emissions from the total industry for 1980 are estimated to be higher than would be projected from the model uncontrolled plant. Table VII-2 shows the emissions estimated for the total industry for 1980 to be 48 kg/hr for benzene and 140 kg/hr for VOC.[3--5] The model plant reflects the processes in operation today with the lowest emission levels and the likely emission level of future processes. Since some of the older processes in operation today inherently have higher emissions, the actual industry emissions are expected to exceed the projection based on the model uncontrolled plant. The areas of deviation from the model plant are noted on Table VII-3.

There are five major emission sources: tail-gas treatment vent, atmospheric distillation vents, vacuum system vent, fugitive vents, and storage and handling vents. The vent from tail-gas treatment, the atmospheric distillation vents, and the vacuum system vent can be either returned to a compatible process step or controlled by processing through a carbon adsorption system. The vent from crystal processing can also be controlled by the above carbon adsorption system. The resultant emission reduction would be about 98.79% for both benzene and total VOC. The estimated capital cost of the carbon adsorption installation is $325,000 and the annual cost, including a $30,618 credit for materials recovered, would be $87,734. The cost effectiveness for benzene would be $1104/Mg, and for total VOC emission reduction would be $613/Mg.

Benzene storage emissions can be controlled by means of internal-floating-roof tanks. The emission reduction would be 85%.

Table VII-1. Emission Summary Model Plant

	Emission Rate (kg/hr)			
	Uncontrolled		Controlled	
Emission Source	Benzene	VOC	Benzene	VOC
Tail-gas treatment	5.7	6.7	0.074	0.087
Atmospheric distillation vents	4.0	4.3	0.045	0.049
Vacuum system vent		5.1		0.066
p-DCB crystallization vent		0.18		0.18
p-DCB crystal processing vent		0.92		0.012
Fugitive	6.4	21.6	1.77	6.77
Storage and handling	4.5	6.33	0.67	2.5
Secondary	0.21	0.33	0.21	0.33
Total	20.81	45.5	2.77	9.99

Table VII-2. Industry Emission Rates at 1980 Production Levels

	Emission Rate (kg/hr)	
	Benzene	Total VOC
Model plant uncontrolled emissions scaled to 1978 demand	39	87
Industry emissions estimated for 1978	48	140

Table VII-3. Emission Ratios for Model Plant and Industry

Emission Source	Uncontrolled Model Plant Emission Ratio (g/kg)		Industry Emissions Ratio (g/kg) Estimated for 1978	
	Benzene	Total VOC	Benzene	Total VOC
Process	0.88	1.56	1.24[a]	3.9[a]
Fugitive	0.58	1.97	0.58	1.97
Storage and handling	0.41	0.57	0.3	0.5
Secondary	0.02	0.03	0.18[b]	0.28[b]
	1.89	4.13	2.3	6.65

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[a] Some industry processes have greater emissions from the heavy-ends discharge (see refs 3,4).

[b] Some industry processes lose benzene and chlorobenzene into the wastewater because of poor phase separation and vacuum jet discharge (see refs 3,5).

REFERENCES*

1. A. C. Guessler, "CEH Product Review on Chlorobenzenes," pp. 633.5030 C-L in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (March 1980).

2. T. C. Gunn *et al.*, "CEH Marketing Research Report on Benzene," pp. 718.5021A-E in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (May 1977).

3. S. W. Dylewski, Hydroscience, Inc., Trip Report on Visit to Natrium Plant of PPG Industries, Inc., March 23, 1978 (data on file at EPA, ESED, Research Triangle Park, NC).

4. C. A. Peterson, Jr., Hydroscience, Inc., Trip Report on Visit Regarding Sauget, Illinois, Plant of Monsanto Co., April 25, 1978 (data on file at EPA, ESED, Research Triangle Park, NC).

5. Response to EPA's request for information on emissions from chlorobenzene manufacturers (data on file at EPA, ESED, Research Triangle Park, NC).

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APPENDIX A

PHYSICAL PROPERTIES OF CHLOROBENZENE, o-DICHLOROBENZENE, p-DICHLOROBENZENE AND BENZENE

Table A-1. Physical Properties of Chlorobenzene*

Synonyms	Phenyl chloride, monochlorobenzene, chlorobenzol
Molecular formula	C_6H_5Cl
Molecular weight	112.56
Physical state	Liquid
Vapor pressure	1618 Pa at 25°C
Vapor specific gravity	3.88
Boiling point	131.7°C
Melting point	-45.6°C
Density	1.1058 g/ml at 20°C/4°C
Water solubility	Insoluble

*From: J. Dorigan et al., "Chlorobenzenes," p. A1-248 in Appendix 1, Rev. 1 (Chemicals A--C), to Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals, MTR-7248, MITRE Corp., McLean, VA (September 1976).

Table A-2. Physical Properties of o-Dichlorobenzene*

Synonyms	DCB, dichlorobenzol
Molecular formula	$C_6H_4Cl_2$
Molecular weight	147.0
Physical state	Liquid
Vapor pressure	193 Pa at 25°C
Vapor specific gravity	5.05
Boiling point	180.5°C
Melting point	-17°C
Density	1.305 at 20°C/4°C
Water solubility	Insoluble

*From: J. Dorigan et al., "o-Dichlorobenzene," p. AII-38 in Appendix II, Rev. 1 (Chemicals D--E), to Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals, MTR-7248, MITRE Corp., McLean, VA (September 1976).

Table A-3. Physical Properties of p-Dichlorobenzene*

Synonyms	DCB, dichlorobenzol
Molecular formula	$C_6H_4Cl_2$
Molecular weight	147.0
Physical state	Solid
Vapor pressure	1333 Pa at 54.8°C
Vapor specific gravity	
Boiling point	173.4°C
Melting point	53°C
Density	1.2475 g/ml at 55°C/4°C
Water solubility	Insoluble

*From: J. Dorigan *et al*., "p-Dichlorobenzene," p. AII-40 in Appendix II, Rev. 1 (Chemicals D--E), to *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Chemicals*, MTR-7248, MITRE Corp., McLean, VA (September 1976).

Table A-4. Physical Properties of Benzene[a]

Synonyms	Benzol, phenylhydride, coal naphtha
Molecular formula	C_6H_6
Molecular weight	78.11
Physical state	Liquid
Vapor pressure	95.9 mm at 25°C
Vapor density	2.77
Boiling point	80.1°C at 760 mm
Melting point	5.5°C
Density	0.8787 at 20°C/4°C
Water solubility	Slight (1.79 g/liter)

[a] J. Dorigan, B. Fuller, and R. Duffy, "Benzene," p AI-102 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals a-c)*, MTR-7248, Rev 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

APPENDIX B

ATMOSPHERIC DISPERSION PARAMETERS

Table B-1. Atmospheric Dispersion Parameters for Model Plant

	Parameters						
	Emission Rate (g/sec)		Height	Diameter	Discharge	Flow	Discharge
Source	Benzene	Total VOC	(m)	(m)	Temperature (K)	Rate (m^3/sec)	Velocity (m/sec
		Uncontrolled Emissions					
Tail-gas treatment caustic scrubber	1.57	1.86	21	0.0381	298	0.00833	7.3
Atmospheric distillation vents							
Benzene drying	0.053	0.053	21	0.025	298	0.000144	0.29
Heavy-ends processing		None	21	0.025	298		
MCB distillation	0.917	1.01	25.9	0.025	298	0.00181	3.7
Benzene recovery	0.133	0.133	21	0.025	298	0.00038	0.77
Vacuum system		1.40	15.2	0.050	333	0.01549	7.9
p-DCB crystallization		0.05	9.1	0.025	348	9.71×10^{-6}	<0.02
p-DCB crystal processing		0.26	9.1	0.46	298	1.29	7.76
Storage and handling							
Wet benzene (2)	0.48(ea)		12.2	14	297		
Wet benzene (2)	0.12(ea)		7.3	6.3	297		
Dry benzene	0.056		7.3	6.3	297		
MCB (2)		0.05(ea)	7.3	6.3	308		
MCB (3)		0.075(ea)	12.2	14	289		
p-DCB, crude (2)		0.029(ea)	4.9	4.9	348		
p-DCB (3)		0.015(ea)	2.4	4.4	348		
p-DCB		0.075	9.8	7.7	348		
p-DCB SG (2)		0.009(ea)	2.4	4.4	348		
o-DCB (2)		0.002(ea)	2.4	4.4	308		
o-DCB		0.009	9.8	10.4	289		
o-DCB SG (2)		0.001(ea)	4.9	3.9	289		
Mixed DCB		0.002	2.4	4.4	308		
TCB (2)		0.002(ea)	2.4	4.4	323		
Fugitive emissions*	1.78	6.01					
Secondary emissions	0.058	0.092					
		Controlled Emissions					
p-DCB crystallization		0.05	9.1	0.025	348	9.71×10^{-6}	<0.02
Storage and handling							
Wet benzene (2)	0.06(ea)		12.2	14	297		
Wet benzene (2)	0.02(ea)		7.3	6.3	297		
Dry benzene	0.018		7.3	6.3	297		
MCB (2)		0.056(ea)	7.3	6.3	308		
MCB (3)		0.084(ea)	12.2	14	289		
p-DCB, crude (2)		0.032(ea)	4.9	4.9	348		
p-DCB (3)		0.016(ea)	2.4	4.4	348		
p-DCB		0.084	9.8	7.7	348		
p-DCB SG (2)		0.010(ea)	2.4	4.4	348		
o-DCB (2)		0.002(ea)	2.4	4.4	308		
o-DCB		0.010	9.8	10.4	289		
o-DCB SG (2)		0.001(ea)	4.9	3.9	289		
Mixed DCB		0.002	2.4	4.4	308		
TCB (2)		0.002(ea)	2.4	4.4	323		
Carbon absorber	0.024	0.048	6	0.5	321	1.78	9.1
Fugitive emissions*	0.496	1.878					
Secondary emissions	0.058	0.092					

---

*Fugitive emissions are evenly distributed over a rectangular area 60 X 150 m.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

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EXISTING PLANT CONSIDERATIONS

Table D-1 lists process control devices reported to be in use by industry. To gather information for the preparation of this report two site visits were made to manufacturers of chlorobenzene products. One site visit included a tour through the facilities,[1] the other only involved a discussion of the process.[2] Data from two other facilities was received in response to request for information by the EPA.[3,4]

PPG Industries, Inc. - New Martinsville, WV

Variations between the PPG process and the model process are: (1) the water leaving the water scrubber (about 120 gpm) is discharged to the river while the vent is emitted to the atmosphere. This results in any VOC that are present in the vent from the HCl gas stream resulting in direct emissions or potential secondary emission; (2) Atmospheric distillation vent pases through a blowdown kettle which is vented through a steam jet, through a crude product surge tank, and finally is vented to the atmosphere through a water-cooled surface condenser; (3) the vacuum distillation system is vented to the atmosphere through a steam jet and water-cooled contact condenser; (4) the p-dichlorobenzene crystalization and crystal processing steps are directly vented to the atmosphere; and the benzene storage tanks are vented directly to the atmosphere. The emissions are shown in Table D-2 and their sources are shown in Fig. D-1.[1] The cost or practicability of retrofit improvement to this process has not been studied.

Monsanto Company, Sauget, IL

Variations between the Monsanto process and the model process are: (1) the water leaving the water scrubber (peak flow of 150 gpm) is discharged to wastewater treatment while the vent is emitted to the atmosphere. This results in any VOC that is present in the vent from the HCl gas stream resulting in direct emission or potential secondary emission; (2) Vents from chlorobenzene distillation is emitted to the atmosphere; (3) the separation of o-dichlorobenzene from p-dichlorobenzene is accomplished by crystalization with the o-dichlorobenzene obtained as product of high purity and the p-dichlorobenzene fraction is a mixture of isomers. The product is transferred or sold without a p-dichlorobenzene crystal purification and handling step and thus does not result in losses attendant to this type of processing. The emissions are shown in Table A-3.[2] The cost or practicability of retrofit improvement to this process has not been studied.

Table D-1. Emission Control Devices Currently Used by Domestic Chlorobenzene Products Industry

Source	Control Devices Used			
	PPG Industries[a]	Monsanto Company[b]	Montrose Corp. of Calif.[c]	Dow Chemical[d]
Tail-gas treatment	Water scrubber	Water scrubber	Water scrubber	Water scrubber, caustic scrubber
Atmospheric distillation	Vent condensers and steam jet after-condenser	Vent condensers	Vent condensers	Vent condensers, venturi scrubber,[e] carbon adsorption[e]
Vacuum system	Steam jet after condenser	N.R.[f]	Steam jet after-condenser	Venturi scrubber
p-DCB crystallization	None	N.R.	N.A.[g]	Carbon adsorption
p-DCB crystal processing	None	N.R.	N.A.	Carbon adsorption[h]
Storage and handling	None	None	N.R.	Vent condenser on benzene storage

[a] See ref 1.

[b] See ref 2.

[c] See ref 3.

[d] See ref 4.

[e] To be installed May 1978.

[f] Not reported.

[g] Not applicable.

[h] Reported to be on crystallization vent. See ref 4.

TABLE D-2
DIRECT EMISSIONS

Stream No.	ECD No.	Pollutant Flow Rate lb/hr/100 Tons/day Products					
		Benzene	MCB	o-DCB	p-DCB	m-DCB	Gas,CFM
1	101	0.017	--	--	--	--	
5	102	8.34	24.3	0.95	1.34	--	
9	103	--	4.0	--	--	--	57
11	104	0.004	0.0117	0.0002	0.0042	--	.0011
15	105	--	--	0.06	6.25	0.26	0.274
20	106	--	--	1.098	--	--	.046
12	Receiver Vent[1]	.01	--	--	--	--	
13	Receiver Vent[1]	--	0.0018	--	--	--	
22	Roof Fan[1]	0.12	0.14	5.54	98.61	--	
		8.49	28.38	7.65	106.2	0.62	

[1] No Emission Control Device present

Montrose Chemical Corporation - Henderson, NV

Variations between the Montrose Chemical process and the model process are: (1) the water leaving the water scrubber (quantity unknown) is presumed to go to wastewater treatment while the vent stream containing benzene (3.9 lb/hr) and chlorinated benzenes (0.76 lb/hr) is emitted to the atmosphere; (2) the vent stream from distillation passes through steam jet ejectors, water-cooled after-condensers, and are emitted to the atmosphere; (3) the dichlorobenzenes are presumed to be sold prior to any further processing. The cost or practicability of retrofit improvement to this process has not been studied.

Dow Chemical USA - Midland, MI

Variations between the Dow Chemical process and the model process are: (1) the vent stream from the caustic scrubber is discharged to the atmosphere, however, the manufacturer stated they planned to install an adsorption bed (presumed to be carbon) in May 1978; (3) the vent streams from distillation pass through steam jet vacuum systems and discharge to the atmosphere; (4) the vent stream from p-dichlorobenzene does go through a carbon adsorption bed, however, not in combination with other process vent streams. The cost or practicability of retrofit improvement to this process has not been studied.

Retrofitting Controls

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

REFERENCES*

1. S. W. Dylewski, IT Enviroscience, Inc., Trip Report on Visit to Natrium Plant of PPG Industries, Inc., March 23, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

2. C. A. Peterson, Jr., IT Enviroscience, Inc., Trip Report on Visit Regarding Sauget, Illinois, Plant of Monsanto Co., April 25, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. H. J. Wurzer, Montrose Chemical Corp. of California, letter dated March 7, 1978, to EPA.

4. J. S. Beale, Dow Chemical Company, letter dated March 14, 1978, to EPA.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

APPENDIX E

COST ESTIMATE PROCEDURE

Emission to Carbon Adsorption (CA)

$$\text{Benzene} = \frac{9.2\ \text{kg}}{\text{hr}} \times \frac{2.2\ \text{lb}}{\text{kg}} \times \frac{\text{hr}}{60\ \text{min}} \times \frac{\text{lb mole}}{78\ \text{lbs}} \times \frac{359\ \text{ft}^3}{\text{lb mole}} = 1.5\ \text{scfm}$$

$$\text{Monochlorobenzene}\ \frac{2.43\ \text{kg}}{\text{hr}}\ \text{at 113 lb/lb mole} = 0.28\ \text{scfm}$$

$$\text{Dichlorobenzene}\ \frac{4.89\ \text{kg}}{\text{hr}}\ \text{at 147 lb/lb mole} = \underline{0.44\ \text{scfm}}$$

Total VOC 2.22 scfm

Air = 5531 kg/hr at 29 lb/lb mole 2510.56 scfm

Total waste gas to CA 2513 scfm

From Fig. IV-1 of the control device evaluation report for carbon adsorption the December 1979 installed capital for 2,500 scfm is $200,000. The pretreatment system requires a 46 ft^2 Karbate heaterchanger to reduce the relative humidity. Since the waste gas is corrosive, adequate protection will be required such as glass-lined pumps, and the use of liners such as epoxy, Haveg, or equivalent. These extra items are estimated to increase the capital cost by $125,000. Total installed capital = $325,000.

With an average VOC molecular weight of ~100 and an estimated loading capacity of 6 lb of VOC/100 lb of carbon, the carbon requirement from CA report Fig. II-1 is 4 lb of carbon/1000 scf. The total carbon requirement is therefore:

$$\frac{4\ \text{lb C}}{1000\ \text{scf}}\quad \frac{2513\ \text{scf}}{\text{min}}\quad \frac{60\ \text{min}}{\text{hr}}\quad \frac{3\ \text{hr}}{\text{cycle}} = \frac{1809\ \text{lb of C}}{\text{cycle}}$$

As indicated by CA report Fig. IV-1, the capital cost includes the carbon for two beds. CA Fig. IV-4 indicates the annual cost to be $32/scfm or $80,416.

The annual cost adjustments for fixed costs associated with added capital, steam for gas conditioning and raw material recovery credits are included in the following cost summary.

Carbon Adsorption Control Cost Summary

	Model Plant		
	2500 scfm	1250 scfm	3750 scfm
Capital from CA report (Fig. IV-1)	$200,000	$150,000	$240,000
Extra capital	125,000	82,469	159,428
Total capital	$325,000	$232,469	$399,428
Fixed cost for extra capital	$ 36,250	$ 23,916	$ 46,234
Steam conditioning	1,686	843	2,529
Benzene credit	(18,468)	(9,234)	(27,702)
Chlorobenzene credit (as raw material)	(12,150)	(6,075)	(18,225)
Annual cost: CA Fig. IV-4	80,416	53,750	101,250
Net annual cost	$ 87,734	$ 63,200	$104,086
Benzene emission reduction 98.7%	79.5 Mg/yr	39.7 Mg/yr	119 Mg/yr
Total VOC reduction 98.7%	143 Mg/yr	72 Mg/yr	214 Mg/yr
Cost effectiveness			
$/Mg of benzene reduced	$1104	$1,592	$875
$/Mg of VOC reduced	$ 613	$ 884	$486

APPENDIX F

LIST OF EPA INFORMATION SOURCES

F. J. Basile, Jr. (Monsanto Co.), letter to C. A. Peterson (Hydroscience, Inc.), March 3, 1978.

C. R. Dilmore, Jr. (PPG Industries), letter to S. W. Dylewski (Hydroscience, Inc.), February 8, 1978.

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J. S. Beale (Dow Chemical Co.), letter to EPA, March 14, 1978.

REPORT 4

MALEIC ANHYDRIDE

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. MALEIC ANHYDRIDE

Maleic anhydride (MA) production was selected for the following reasons: preliminary estimates indicated that emissions of volatile organic compounds (VOC) are relatively high; the predominant manufacturing process emits large quantities of benzene, which was listed as a hazardous pollutant by the EPA in the Federal Register on June 8, 1977; and the product growth is expected to be higher than the industry average.

MA is solid at ambient conditions (see Appendix A for pertinent physical properties) although it generally exists in the process as a liquid (molten MA) or as maleic acid. The predominant emission, benzene, however, is a volatile liquid at ambient conditions but is emitted as a gas.

B. MA USAGE AND GROWTH

Table II-1 shows MA end uses and the expected growth rate. The major end use is the production of unsaturated polyester resins, which are used in reinforced-plastic applications such as marine craft, building panels, automobiles, tanks, and pipes.

The domestic MA production capacity for 1979 was reported[1] to be 214,000 Mg, with approximately 70% of this capacity being utilized in 1978. Based on the assumption of an 8% annual growth in MA consumption, production will reach approximately 96% of the present capacity by 1982. No shortage of benzene, the major raw material, is expected during this period.

C. DOMESTIC PRODUCERS

As of 1978 there were eight domestic facilities producing MA in ten plants. Table II-2 lists the producers and the processes being used; Fig. II-1 shows the plant locations. Approximately 83% of the 214,000-Mg/yr domestic capacity is based on the oxidation of benzene. Oxidation of n-butane accounts for another 15% of capacity, and the remaining 2% is from phthalic anhydride production, which gives MA as a by-product.[1] The projected growth rate for the n-butane oxidation process through 1982 is 24%, primarily through conversion, compared to an overall maleic anhydride expected growth rate of 8%. Data regarding the

Table II-1. Maleic Anhydride Usage and Growth[a]

End Use	Production (%)	Average Annual Growth (%)
Unsaturated polyester resins	56	9
Fumaric acid	5	4
Agricultural chemicals	8	6
Alkyd resins	1	0
Lubricating additives	9	9
Copolymers	6	8
Maleic acid	4	8
Chlorendic anhydride and acid	2	10
Other	9	17
	100	

[a] See ref 1.

Table II-2. Maleic Anhydride Capacity[a]

Company	Location	Production Capacity as of 1979 (10^3 Mg)	Process
Amoco	Joliet, IL	27	b
Ashland	Neal, WV	27	c
Koppers	Bridgeville, PA	0[d]	c
	Chicago, IL	5	e
Monsanto	St. Louis, MO	48	c (80%) b (20%)
Denka (Petro-Tex)	Houston, TX	23	c
Reichhold[f]	Elizabeth, NJ	14	c
	Morris, IL	20	c
Tenneco	Fords, NJ	12	c
U. S. Steel	Neville Island, PA	38	c
Total		214	

[a] See ref 1.

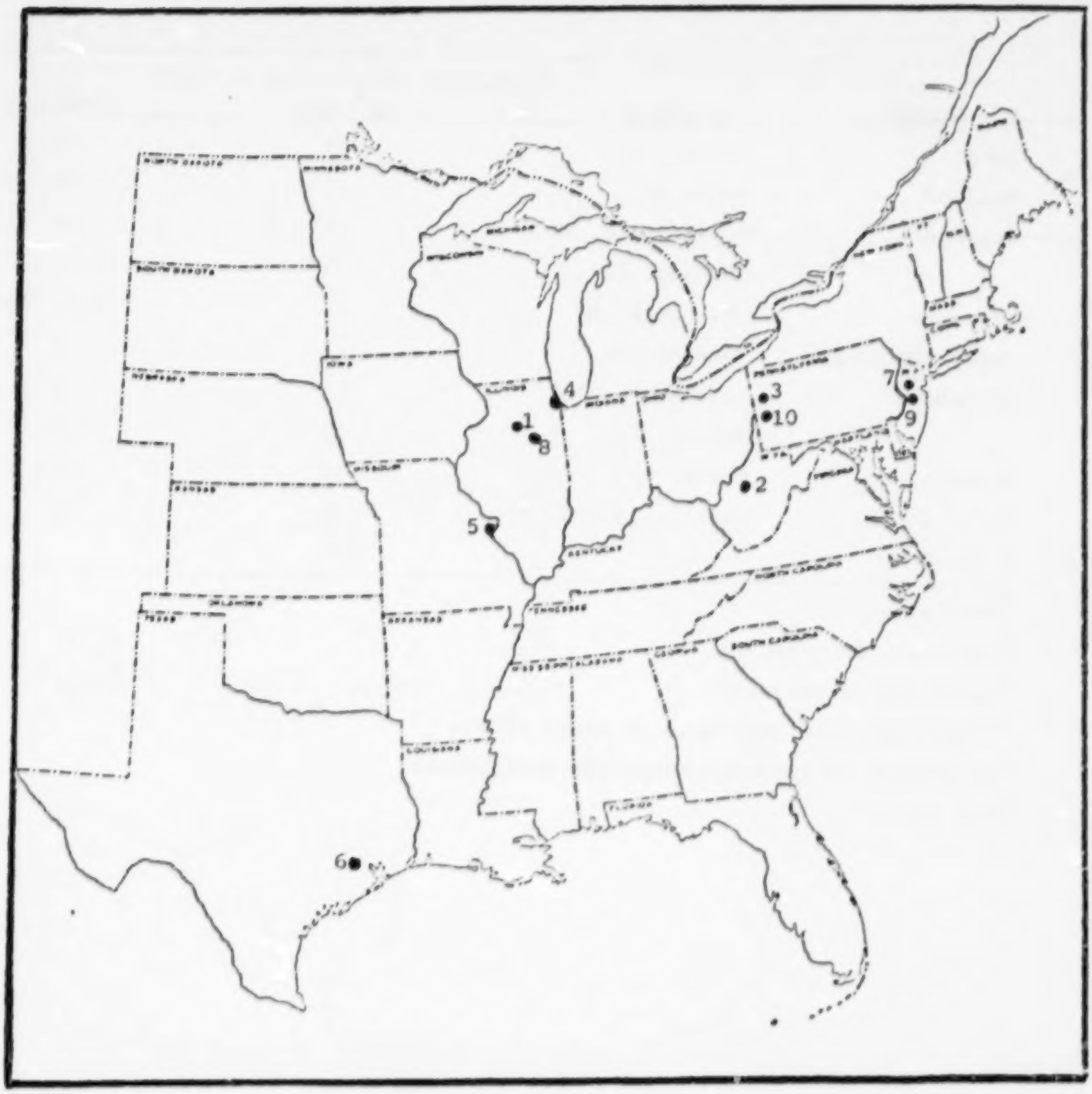
[b] Oxidation of *n*-butane.

[c] Oxidation of benzene.

[d] 15,000-Mg plant shut down in April 1979.

[e] By-product of phthalic anhydride manufacture.

[f] See ref 6.



1. Amoco, Joliet, IL
2. Ashland, Neal, W. VA
3. Koppers, Bridgeville, PA
4. Koppers, Chicago, IL
5. Monsanto, St. Louis, MO
6. Denka (Petro-Tex), Houston, TX
7. Reichhold, Elizabeth, NJ
8. Reichhold, Morris, IL
9. Tenneco, Fords, NJ
10. U.S. Steel, Neville Island, PA

Fig. II-1. Manufacturing Locations of Maleic Anhydride

economic incentives for switching to n-butane oxidation are not available. No growth in the quantity of MA recovered during phthalic anhydride production is expected.[2]

In 1960 work began on developing a catalyst suitable for producing MA from butane/butene (C_4) streams available from naphtha cracking. This effort was curtailed during the 1961—1967 period, when the MA market was depressed and low-cost benzene was available. In 1967 demand for MA increased, and work was renewed in Japan by Kasei Mizuishima; in 1974 announcements concerning the production of MA from C_4s were made by Petro-Tex, Chem Systems, BASF, Bayer, Alusuisse/UCB, and Mitsubishi.[2] Presently, Amoco and Monsanto are producing MA from an n-butane feedstock.[1] The main drawback of the n-butane process is the unavailability of a catalyst that provides competitive yields.[3]

Companies that product MA are listed below:

1. Amoco Chemicals Corporation

   Amoco has the only domestic plant totally dedicated to the n-butane process.[1] It has an annual capacity of 27,000 Mg and is reportedly expansible to 41,000 Mg.[3]

2. Ashland Chemical Company

   The Ashland facility is a benzene-based plant with an annual capacity of 27,000 Mg and is expansible to 41,000 Mg.[1] This plant can be switched from benzene to n-butane feedstocks.[3]

3. Koppers Company, Inc.

   Koppers announced that their 15,000-Mg/yr benzene oxidation plant was shut down in April 1979. Their Chicago facility can recover 5000 Mg of MA per year from the effluent of their phthalic anhydride plant, which was started in 1975.[1]

4. Monsanto Company

   Monsanto with a capacity of 48,000 Mg/yr is the largest producer of MA. Some MA is consumed captively to produce fumaric acid, maleate/fumerate esters, styrene copolymers, and ethylene-maleic anhydride copolymers. Monsanto plans to start up a 46,000-Mg butane-based plant in Pensecola, FL, in 1983.[1]

5. Denka USA

Denka's 23,000-Mg/yr Houston facility was designed by Scientific Design Company, Inc., and was purchased from Petro-Tex Chemical Corporation on July 1, 1977.[4] They have a current permit from the Texas Air Control Board to operate an n-butane reactor.[5]

6. Reichhold Chemicals, Inc.

Reichhold's combined production from their Elizabeth, NJ, and Morris, IL, plants is 34,000 Mg/yr, some of which is used captively to produce unsaturated polyester resins, alkyd resins, and plasticizers.[1,6]

7. Tenneco Chemicals, Inc.

A small part of Tenneco's 12,000-Mg/yr MA production is used captively to produce fumaric acid, dibutyl maleate, and dodecanyl-succinic anhydride.[1]

8. United States Steel Corporation

The MA capacity of U.S. Steel was expanded to 38,000 Mg/yr.[3] Some of their MA production is used captively to produce fumaric acid, dibutyl maleate, and dioctyl maleate.[1]

9. Allied Chemicals Corporation

Allied ceased production in 1974 of MA at their Moundsville, WV, plant, which had a capacity of 900 Mg/yr.[1].

The expansion capabilities of 14,000 Mg each for Amoco and Ashland plus the 46,000-Mg new Monsanto plant represent a potential nationwide capacity of 288,000 Mg per year.

D. REFERENCES*

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3. "Maleic Makers Build on Hopes for Polyester," Chemical Week, pp 37 and 38 (Feb. 2, 1977).

4. Personal communication Nov. 17, 1977, between J. F. Lawson, IT Enviroscience, Inc., and R. E. Hinkson, Denka USA.

5. Permit Exemption Request from R. D. Pruessner, Petro-Tex Chemical, to Charles Barden, Texas Air Control Board, Feb. 23, 1976.

6. P.S. Hewett, Reichhold Chemicals, Inc., letter dated Mar. 27, 1978, to D. P. Patrick, EPA.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTIONS

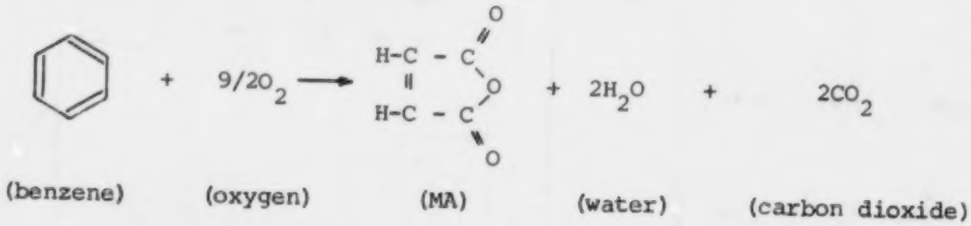
A. INTRODUCTION

As discussed in Sect. II, the two major processes used to manufacture maleic anhydride (MA) in the United States are benzene oxidation and butane oxidation. A small amount of MA is recovered as a by-product of phthalic anhydride production. The only significant foreign process for MA production not used in the United States starts with a butene mixture feedstock. This process is operated in France[1] and Japan.[2] There are no known plans to introduce this process domestically.

B. BENZENE OXIDATION PROCESS

1. Basic Process

MA is produced by the following chemical reaction:



The process flow diagram shown in Fig. III-1 represents a typical process, which is continuous; however, some plants operate batchwise. The emissions in either case are judged to be the same.[3]

A mixture of vaporized benzene and air enters a tubular fixed-bed reactor, where the catalytic oxidation of benzene is carried out at a temperature of 350 to 400°C. The catalyst contains approximately 70% vanadium pentoxide supported on an inert carrier; most of these systems also contain 25 to 30% molybdenum oxide. The reaction is highly exothermic, releasing 24.4 MJ/kg of reacted benzene, with the excess heat being used to generate steam. MA yields range from 60 to 67% of theoretical.[3]

The reactor feed mixture contains an excess of air because benzene is explosive in air at concentrations above 1.5 vol %. The resulting large volume of reactor exhaust (stream 3) dictates the size of subsequent product recovery equipment.

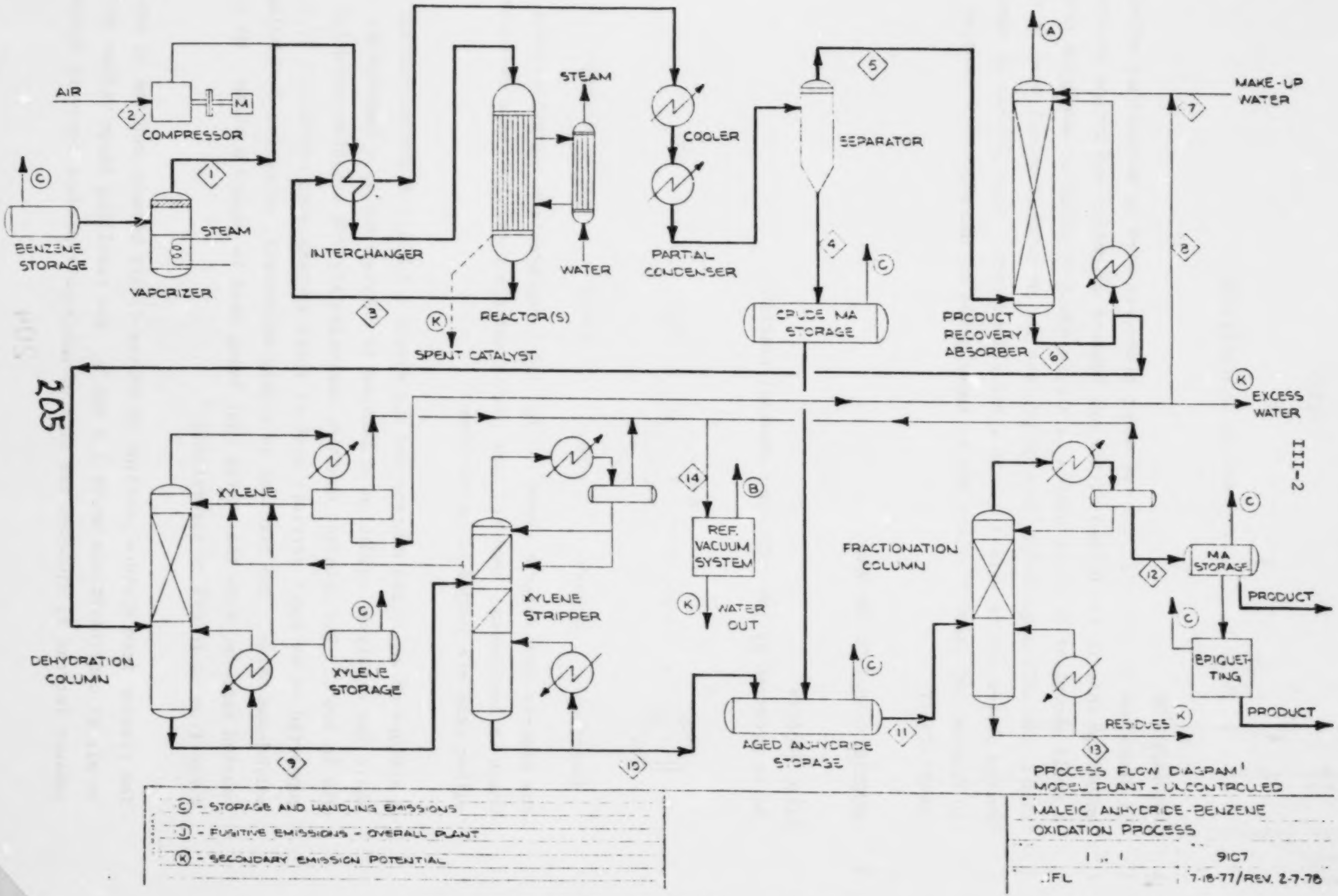

AIR
2
COMPRESSOR
M
C
BENZENE STORAGE
1
VAPORIZER
STEAM
INTERCHANGER
3
K
SPENT CATALYST
REACTOR(S)
STEAM
WATER
COOLER
PARTIAL CONDENSER
SEPARATOR
5
4
C
CRUDE MA STORAGE
A
PRODUCT RECOVERY ABSORBER
6
MAKE-UP WATER
7
8
K
EXCESS WATER
XYLENE
DEHYDRATION COLUMN
C
XYLENE STORAGE
9
XYLENE STRIPPER
10
14
B
REF. VACUUM SYSTEM
K
WATER OUT
C
AGED ANHYDRIDE STORAGE
11
FRACTIONATION COLUMN
12
C
MA STORAGE
PRODUCT
C
BRIQUETTING
PRODUCT
RESIDUES
K
13
C - STORAGE AND HANDLING EMISSIONS
J - FUGITIVE EMISSIONS - OVERALL PLANT
K - SECONDARY EMISSION POTENTIAL
PROCESS FLOW DIAGRAM
MODEL PLANT - UNCONTROLLED
MALEIC ANHYDRIDE-BENZENE
OXIDATION PROCESS
9107
JFL
7-18-77/REV. 2-7-78

Fig. III-1. Maleic Anhydride - Model Plant

The stream passes through a cooler, partial condenser, and separator, in which 40% of the MA is condensed and separated as crude MA (stream 4).[4] The remaining vapor (stream 5) enters the product recovery absorber, where it is contacted with water or aqueous maleic acid. The absorber product (stream 6) is a 40 wt % aqueous solution of maleic acid. The absorber vent (A) exhausts to the atmosphere or is directed to an emission control device.[3]

The 40% maleic acid (stream 6) is dehydrated by azeotropic distillation with xylene. Any xylene retained in the crude MA (stream 9) is removed by the xylene stripping column, and the crude MA (stream 10) from this column is combined with the crude MA (stream 4) from the separator.

Crude MA is aged, which causes any color-forming impurities to polymerize. After aging, the crude MA (stream 11) is fed to the fractionation column, which yields molten MA as the purified overhead product (stream 12). A small percentage is taken an additional step for sale as briquets. The fractionation column bottoms containing the color-forming impurities are removed as liquid residue waste (stream 13). This stream either becomes part of the untreated effluent or is fed to a liquid incinerator.[3]

The vacuum lines from the dehydration column, xylene stripper, and fractionation column are joined (stream 14) to the vacuum system. The refining vacuum system vent (B) can exhaust to the atmosphere, recycle (stream 5) to the product recovery absorber, or be directed to an emission control device. Water from the vacuum system can be recycled as makeup water (stream 7) or join the liquid residue waste (stream 13).[3]

Essentially all process emissions will exit through the product recovery absorber (vent A). These emissions will include any unreacted benzene, which can constitute 3 to 7% of the total benzene feed.[5] The only other process emission source is the refining vacuum system vent (vent B), which can contain small amounts of MA and xylene.

Fugitive emissions throughout the process can contain benzene, xylene, MA, and maleic acid. Corrosion problems due to leaks caused by maleic acid can increase fugitive emissions. As with most organic chemical processes, leaks into cooling water could occur and allow volatile organic compounds (VOC) to escape as a fugitive emission.

Storage and handling emission sources (labeled C on Fig. III-1) include benzene, xylene, MA, and crude-MA storage, plus emissions from the briquetting operation.

There are four potential sources of secondary emissions (labeled K on Fig.III-1): spent reactor catalyst, excess water from the dehydration column, vacuum system water, and fractionation column residues. The small amount of residual organics in the spent catalyst after it is washed has a low vapor pressure and produces no significant emissions. Xylene is the principal organic contamination in the excess water from the dehydration column and the vacuum system water. Residues from the fractionation column are relatively heavy organics with a molecular weight greater than 116 and produce no significant secondary emissions.

2. Process Variations

In place of the partial condensation system (cooler, partial condenser, and separator) shown in Fig. III-1, a so-called switch condenser system can be incorporated. This utilizes a series of condensers that are alternately cooled to freeze solid MA on the surface and then heated to melt the MA for pumping to crude-MA storage. Switch condensing can remove up to 60% of the MA from the process, compared to 40% removed by the partial condensation system.[6] The removal of additional MA would allow the size of the product recovery absorber to be reduced and would slightly reduce the maleic acid loss through the product recovery absorber (vent A).

Xylene is the only known azeotropic agent currently being used for dehydration. Several other agents can be used, including isoamyl butyrate, di-isobutyl ketone, anisole, and cumene.[3]

A vacuum evaporation system, which replaces the dehydration column and xylene stripper, is used by at least one plant to remove water and to dehydrate the maleic acid to form MA.[6] Since an azeotropic agent is no longer required, xylene is eliminated from process emissions.

C. n-BUTANE OXIDATION

All process data concerning the n-butane oxidation process are currently proprietary and unavailable. A benzene oxidation process can be converted to n-butane oxidation by changing the catalyst system; this conversion can be done for much less than the cost of a new plant. However, the converted process would be less efficient than a new n-butane process because reaction conditions are not optimum. The lowered efficiency might be serious enough to warrant other major design changes.[7]

A major advantage of this process is that there are no benzene emissions. Other VOC emissions should not differ to a great extent from the benzene oxidation process.[5]

D. PHTHALIC ANHYDRIDE BY-PRODUCT PROCESS

Phthalic anhydride is manufactured from naphthalene and ortho-xylene. Maleic anhydride is recovered as a by-product from the plant effluent.[3] The emissions associated with MA recovery are believed to be insignificant and are not being investigated at this time.

E. FOREIGN PROCESSES (MIXED BUTENES)

1. Basic Process

The only significant deviation from benzene oxidation for MA production in foreign processes is the use of feedstocks of 65 to 80% n-butenes, with the remainder being mostly butanes or isobutene. The general process description is very similar to that shown in Fig. III-1 for benzene oxidation and therefore is not repeated here.[1,2]

The exhaust from the main process vent contains unreacted butane, butene, and carbon monoxide and various secondary products. Except for the absence of benzene the emissions should be about the same as those for the benzene oxidation process.[5]

2. Process Variations

The most significant process variation is the use of a fluidized catalyst bed rather than a fixed bed. This variation provides good temperature control within the bed and thus allows optimum ratios of butene/air. In contrast optimum benzene/air ratios cannot be used with fixed-bed systems because excess air is necessary for the processes to stay below the explosive range. The reduction of excess air in the fluidized-bed feed will reduce emissions from the product recovery absorber; however, the product yields with the fluidized bed are not as good as with the fixed bed.[8]

D. REFERENCES*

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4. J. F. Lawson, IT Enviroscience, Inc., Trip Report for Visit to Denka Chemical Corp., Houston, TX, Nov. 17, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

5. W. A., Lewis, Jr., G. M. Rinaldi, and T. W. Hughes, Monsanto Research Corp., Source Assessment: Maleic Anhydride Manufacture (received January 1978).

6. J. F. Lawson, IT Enviroscience, Inc., Trip Report for Visit to Reichhold Chemicals, Inc., Morris, IL., July 28, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

The process emission estimates for the benzene oxidation model plant are based on the emissions which were reported in the Houdry study, SRI, a trip report on a visit to Reichhold, and an understanding of the process chemistry and yields.

A. BENZENE OXIDATION PROCESS

1. Model Plant

The model plant* for this study has a capacity of 22,700 Mg/yr (50×10^6 lb/yr), based on 8760** annual hours of operation. Although not an actual operating plant, it is typical of most plants. The model benzene oxidation process, shown in Fig. III-1, best fits today's maleic anhydride manufacturing and engineering technology. Single-process trains as shown are typical for the large plants except for the reaction area, where multiple reactors are common. The model process uses partial condensation and azeotropic drying with xylene.

Typical raw-material, intermediate, and product storage-tank capacities were estimated for a 22,700-Mg/yr plant. The storage-tank requirements are covered under storage emissions. Estimates of potential fugitive sources were based on an equipment count from existing facilities. Characteristics of the model plant important to air-dispersion modeling are shown in Appendix B.

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*See p I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations the error introduced by assuming continuous operation is negligible.

2. Sources and Emissions

All emission rates and sources for the benzene oxidation process are summarized in Table IV-1; part of the data in the table are from refs 1—4.

a. Main Process Vent—The largest vent is the main process vent (A, Fig. III-1) from the product recovery absorber. All plants have this vent. The emission is influenced by the excess air fed to the reactor to maintain the benzene concentration below the explosive limit. The composition of this emission for the model plant is shown in Table IV-2.[1—3] The majority of the unreacted benzene is contained in this stream.

Process upsets that cause more benzene release will affect benzene emissions since the absorber can remove benzene only up to its solubility level in water. These upsets can cause short-duration benzene and VOC emissions of 3 to 5 times the normal amounts. Process startup also increases benzene emissions 3 to 5 times the normal amount because of incomplete benzene reaction. Shutdown will not affect emissions because benzene is shut off as the first step in the shutdown procedure. As a result the level of unreacted benzene emitted from the reactor is immediately reduced.[5]

b. Refining Vacuum Vents—The refining vacuum system vent (B, Fig. III-1) exhausts the noncondensibles from the three vacuum columns used to dehydrate and fractionate MA. The emissions from this vent are affected by the use of inert gases bled into the system for vacuum control and by process leaks into the system. The VOC emission will be maleic acid or xylene and is estimated to be relatively insignificant, as is indicated in Table IV-1. Process upsets, startups, and shutdowns do not affect the VOC emissions from this vent.[3]

c. Fugitive Emissions—Process pumps and valves are potential sources of fugitive emissions. The model plant is estimated to have 15 pumps handling VOC, 3 of which handle benzene. All remaining pumps handle essentially heavy liquids. The estimated number of valves is 500, with 75 controlling benzene vapor, 100 controlling benzene liquid, and 325 controlling heavy liquids. The fugitive-emission factors from Appendix C were applied to this valve and pump count to determine the fugitive emissions shown in Table IV-1.

Table IV-1. Benzene and Total VOC from Uncontrolled Emissions from Production of Maleic Anhydride in Model Plant (22,700-Mg/yr Capacity)

Emission Source	Designation (Fig. IV-1)	Emission Ratio (kg/kg X 10^{-3})[a]		Emission Rate (kg/hr)[b]	
		Benzene	Total VOC	Benzene	Total VOC
Product recovery absorber[c]	A	67.0	86.0	173	224
Refining vacuum system[d]	B		0.1		0.28
Storage and handling[e]	C	1.23	1.27	3.2	3.3
Fugitive[f]	J	1.13	1.24	2.93	3.23
Secondary	K		0.11		0.3
Total		69×10^{-3}	89×10^{-3}	179.0	230.0

[a] kg of emission per kg of maleic anhydride produced.

[b] Emission rates are annual averages at 8760 hr/yr.

[c] See refs 1—3.

[d] See ref 3.

[e] See ref 4.

[f] See Appendix C.

Table IV-2. Waste Gas Composition—Product Recovery Absorber[a] (Weighted Average)

Component	Amount (wt %)	Emission Rate (kg/hr)
Oxygen	16.67	12,603
Nitrogen	73.37	55,470
Carbon dioxide	3.33	2,517
Carbon monoxide	2.33	1,761
Water	4.00	3,025
Benzene	0.23	173
Maleic acid	0.01	7
Formaldehyde	0.05	37
Formic acid	0.01	7
		75,600

[a] See refs 1—3.

d. Storage and Handling Emissions—Emissions result from the storage and handling of benzene, maleic anhydride, and xylene. For the model plant the sources (C) are shown on the flow diagram in Fig. III-1. Storage-tank data for the model plant are given in Table IV-3. The emissions in Table IV-1 were calculated based on fixed-roof tanks, one-half full, on a 11°C diurnal temperature variation, and on the emission equations from AP-42.[4] However, breathing losses were divided by 4 to account for recent evidence[6] indicating that the AP-42 breathing-loss equation overpredicts emissions.

Benzene freezes at 5.5°C; therefore storage tanks are generally heated to maintain the temperature above freezing. Maleic anhydride freezes at 52.8°C; therefore the finished product is normally stored at 60°C and in-process material is stored at 60 to 105°C.

The equations in AP-42[4] were used to calculate the emissions from loading bulk maleic anhydride into tank cars and trucks. These emissions, included in the storage and handling emissions (Table IV-1), are 0.02 kg/hr. Maleic anhydride dust is produced in the briquetting operation but is not a significant atmospheric emission.

e. Secondary Emissions—Secondary emissions of VOC can result from the handling and disposal of process-waste liquid and solid streams. For the model plant four potential sources (K) are indicated on the flow diagram, Fig. III-1.

The spent catalyst removal and reclamation do not present a significant emission potential because the catalyst is thoroughly purged and washed before it is removed. Reclamation is normally done off-site.[2]

For the model plant, aqueous effluent from the vacuum system is estimated to be 417 kg/hr, of which 0.05 kg/hr is xylene. The fractionation column residue stream is 27 kg/hr of low-vapor-pressure organics. Even untreated, these streams do not represent significant emissions. In at least one operating facility, incineration is used to destroy the organics in these liquid streams.[2] With it assumed that there is a well-designed liquid incinerator with 99% destruction of organics, the secondary VOC emissions from this incinerator would be 0.27 kg/hr. Whether liquid incineration or terminal wastewater treat-

Table IV-3. Model-Plant Storage

Content	Tank Size (m^3)	Turnovers Per Year	Bulk Liquid Temp. (°C)
Benzene	2460	12.5	13
	75	410	13
Maleic anhydride	380	40	77
	190	80	71
	380	40	60
Xylene	150	12	13

ment is used, the emission will be no greater than 0.27 kg/hr; this emission rate is included in uncontrolled emissions, Table IV-1.

B. n-BUTANE PROCESSES

As stated earlier, no benzene emissions are associated with the n-butane process. In all other respects the VOC emissions are believed to be about the same as those from the benzene oxidation process, although there are no public data to support this statement.

C. PHTHALIC ANHYDRIDE BY-PRODUCT PROCESSES

The emissions associated with MA recovery are believed to be insignificant and are not being investigated at this time.

D. REFERENCES*

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6. E. C. Pulaski, TRW, Inc., letter dated May 30, 1979 to Richard Burr, EPA.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. BENZENE OXIDATION PROCESS

1. Main Process Vent

A carbon adsorption system or an incineration system can be used to effectively control process emissions. It is assumed that the vent from the refining vacuum system is combined with the main process vent. Therefore treatment of the product recovery absorber vent stream will control all process emissions.

a. Carbon Adsorption——In order to use carbon adsorption the exhaust gas stream must be scrubbed with caustic to remove organic acids and water-soluble organics. Benzene is essentially the only remaining VOC. The stream is then conditioned by heating to reduce the relative humidity. Three carbon beds are specified for the model plant. The exhaust stream passes through two parallel beds while the other bed is being regenerated with steam. The steam condensate is decanted to separate the benzene for recycle to the process, and the benzene-saturated aqueous layer is recycled to the product recovery absorber.

Based on engineering experience with similar applications it was concluded that a carbon adsorption system can be designed and operated at a sustained removal efficiency of greater than 99%. A removal efficiency of 99% was used to project the final emissions from the controlled model plant (Table V-1). The cost of this system is shown in Table VI-1 in Sect. VI. One carbon adsorption system is currently being used to recover benzene from an MA operation, but reportedly has achieved only 85% removal efficiency.[1]

The application of carbon adsorption to control VOC emissions is discussed in the control device evaluation report on carbon adsorption [2]

b. Incineration——The direct fire incineration system for the model-plant waste gas stream has a knockout demister tank to protect the incinerator by preventing liquid stream from reaching the firing area, an incinerator with a combustion chamber of sufficient volume to give a retention time of 0.75 sec, and a stack designed for a velocity of 10 m/sec.[3] Supplemental natural gas and makeup air are required to maintain the necessary combustion temperatures. Heat recovery

Table V-1. Benzene and Total VOC from Emissions Controlled by Carbon Adsorption in the Production of Maleic Anhydride in Model Plant (22,700-Mg/yr Capacity)

Emission Source	Stream Designation (Fig. IV-1)	Control Device or Technique	Emission Reduction (%)	Emission Ratio (kg/kg X 10^{-5})[a,b]		Emission Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
Product recovery absorber	A	Carbon adsorption	99	67	67	1.73	1.73
Refining vacuum system	B	Vent through absorber	99				
Storage and handling[c]	C	Floating-roof tanks (benzene)	85	18	18	0.48	0.48
	C	Scrubber (MA)	99+				
	C	Xylene (none)	0				
Fugitive[d]	J	Detection and correction of major leaks		21	34	0.54	0.88
Secondary	K	None		Trace	11	—	0.3
Total				106 X 10^{-5}	130 X 10^{-5}	2.75	3.39

[a] kg of emission per kg of maleic anhydride produced.

[b] The VOC emission from carbon adsorption is essentially benzene since all other VOC are removed by the caustic scrubber prior to the carbon adsorber.

[c] Approximately 65% of the storage emissions does not vary with production rate.

[d] Fugitive emissions do not vary with production rate.

can be used for steam generation or for preheating the feedstream and thereby reducing natural-gas requirements. Since the waste gas contains corrosive organic acids, stainless steel is specified for construction ahead of the combustion chamber.

Based on engineering experience with similar incineration applications it was concluded that a properly designed and operated incinerator will result in sustained benzene and VOC removal efficiencies of greater than 99%. A removal efficiency of 99% was used to project final emissions from the controlled model plant (Table V-2).

A temperature of 871°C (1600°F) is specified to ensure complete combustion of the waste gas. While it is conceivable that greater than 99% VOC removal could be obtained at lower temperatures, it cannot be dependably predicted. This determination is consistent with government air-pollution engineering manuals.[3],[4] Although the manuals contain no data on combustion temperatures above 800°C, extrapolation of the data presented combined with similar incineration experience justifies the projection of greater than 99% removal at 871°C. The high carbon monoxide content of the waste gas must be considered. Similar incineration experience indicates that the high temperature specified is necessary to obtain acceptable oxidation of the carbon monoxide, as well as complete VOC oxidation. The cost of incorporating this system is shown in Table VI-3.

An incineration system used for VOC removal from an MA process reportedly operates with a combustion temperature of 760°C and achieves a removal efficiency of 93%.[5] An incinerator designed for 871°C can be operated at lower temperatures if it is determined by operating experience that a lower temperature will still provide adequate removal of benzene, VOC, and carbon monoxide.

The application of incineration for VOC emission control is covered in a control device evaluation report for thermal oxidation.[6]

c. Catalytic Incineration——One company is using a catalytic incinerator to control emissions from the product recovery absorber. Very little design data are available. The maximum practical achievable VOC removal efficiency that is

Table V-2. Benzene and Total VOC from Emissions Controlled by Incineration in the Production of Maleic Anhydride in Model Plant (22,700-Mg/yr Capacity)

Emission Source	Stream Designation (Fig. 2)	Control Device or Technique	Emission Reduction (%)	Emission Ratio (kg/kg X 10^{-5})[a]		Emission Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
Product recovery absorber	A	Incineration	99	67	86	1.73	2.24
Refinery vacuum vent	B	Vent through incinerator	99				
Storage and handling[b]	C	Floating-roof tank (benzene)	85	18	18	0.48	0.48
	C	Scrubber (MA)	99+				
	C	Xylene (none)					
Fugitive[c]	J	Detection and correction of major leaks		21	34	0.54	0.88
Secondary	K	None		—	11	—	0.3
Total				106	146	2.75	3.89

[a] kg of emission per kg of maleic anhydride produced.

[b] Approximately 65% of the storage emissions does not vary with production rate.

[c] Fugitive emissions do not vary with production rate.

achievable is reported to be less than 95%. The high catalyst volume or high-temperature requirement makes the unit uneconomical for greater removal efficiencies.[7]

The application of catalytic oxidation for VOC emission control is covered by a control device evaluation report for catalytic oxidation.[8]

d. n-Butane Process—Since the n-butane oxidation process has no potential benzene emissions, conversion to the n-butane process for MA production is an option for benzene emission control. No data are presently available on the control device options for the n-butane process. Also, no data are currently available for comparing the economics of MA production by n-butane oxidation with that by benzene oxidation.

2. Refining Vacuum Vent

The refining vacuum vent is controlled by joining the waste stream ahead of the product-recovery-absorber control device or by joining the product-recovery-absorber feed stream. The incremental costs are relatively small since only piping additions are required, and no added utilities, manpower, or other operating costs are involved. Emissions from the refining vacuum system vent are included in all control system calculations.

3. Fugitive Sources

Controls for fugitive sources are discussed in a separate EPA report[9] covering fugitive emissions for the entire synthetic organic chemicals manufacturing industry. Control of emissions from pumps and valves can be attained by an appropriate leak detection system followed by repair maintenance. Controlled fugitive emissions have been calculated with the use of the factors given in Appendix C and are included in Tables V-1 and V-2. The factors are based on the assumption that major leaks are detected and corrected.[9]

4. Storage and Handling Sources

a. Benzene Storage—Control of benzene storage emissions is covered in a separate EPA document.[10] Information on MA manufacturing locations indicates that benzene is stored in floating-roof tanks at three locations and in fixed-roof tanks at the others.[7] A floating roof* is commonly used to control storage-tank emissions for VOCs in the vapor pressure range of benzene and is used in the model plant instead of fixed-roof tanks. Controlled storage emissions were calculated by assuming that a contact type of internal floating roof with secondary seals would reduce fixed-roof-tank emissions by 85%.[11]

An alternative control method may be possible in MA plants: the fixed-roof storage-tank vents could be tied into the main-process-vent control. The resulting emission reduction should be 99%, which is better than that of a floating-roof tank. However, this modification may add a safety hazard because benzene storage vapors may be in the flammable range.

b. Maleic Anhydride Storage and Handling——The vapor pressure of MA at storage conditions in the model plant is 550 to 1170 Pa; this results in calculated average emissions from fixed-roof tanks of only 0.3 kg/hr. At two production plants the tank vents (as well as air handling from the briquetting operation) are treated in aqueous scrubbers.[1,12] The effluent water is discharged to the sewer. The scrubbers are primarily for plant housekeeping to prevent solid MA buildup rather than for emission reduction. It is estimated that scrubber efficiency under these conditions should be at least 99%. The controlled VOC emissions given in Tables V-1 and V-2 were calculated based on this efficiency.

At one plant the crude maleic anhydride is stored at 130°C and the vent is treated in a xylene scrubber with a stated efficiency of 50%.[13] The xylene effluent can be recycled to the process for MA recovery. This control option may not be adequate without an aqueous scrubber to prevent the resulting MA emission from creating a housekeeping problem associated with a condensed MA solid.

c. Xylene Storage——The calculated emissions from xylene storage in fixed-roof tanks for the model plant average less than 0.03 kg/hr, which is insignificant relative to other emissions from the process; therefore it was assumed that control is not needed.

*Consist of internal floating covers or covered floating roofs as defined in API-2519, 2d ed., 1976 (fixed-roof tanks with internal floating device to reduce vapor loss).

5. Secondary Sources

Secondary emissions are also insignificant. In plants where a liquid incinerator is used to destroy organic effluents the design must be adequate to ensure essentially complete combustion.

6. Current Emission Control

The control devices currently being used by domestic MA producers are given in Appendix E.

B. OTHER PROCESSES

Data are not currently available to size emission control devices for other processes. The only other significant domestic process, n-butane oxidation, is considered to be a control option for benzene emissions.

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10. D. G. Erickson, IT Enviroscience, Inc., Storage and Handling (in preparation for EPA, ESED, Research Triangle Park, NC).

11. Letter dated Aug. 15, 1979, from William T. Moody, TRW, Inc., to David Beck, EPA.

12. Houdry Division of Air Products, Inc., Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry-Maleic Anhydride, prepared for EPA.

13. Permit Exemption Request from R. E. Pruessner, Petro-Tex Chemical, to Charles Borden, Texas Air Control Board, Feb. 23, 1976.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. CONTROL COST IMPACT

The purpose of this section is to present estimated costs and cost-effectiveness (CE) ratios for the control of benzene and total VOC emissions resulting from the production of maleic anhydride. Details of the model plant (Fig. III-1) have been covered in Sects. III and IV. Criteria have been established for control of the VOC process emissions (main process vent combined with refining vacuum) by carbon adsorption and incineration. The capital and annual costs presented for these control systems were obtained from the control device evaluation report for carbon adsorption[1] and for thermal oxidation.[2]

Basis for Capital Cost Estimate——The capital cost estimates represent the total investment required to purchase and install all equipment and material to provide a complete control system performing as defined for a new installation at a typical location. These estimates do not include the cost of MA production lost during installation, the costs for research and development, or the cost for purchase of the land required.

Basis for Annual Cost Estimates——Estimates for annual costs for control alternatives include utilities, operating labor, maintenance supplies, chemicals or raw materials, recovery credit, capital recovery, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. Recovery credits are based on the market value for the material recovered. Chemical or other raw-material costs are based on the market value for the material required.

Carbon loading	<6 kg of VOC/100 kg of carbon
Steam for regeneration	20 kg/kg of organic adsorbed
Steam for gas conditioning	[825 kg/hr (1819 lb/hr)]
50% caustic solution for scrubber	37 kg/hr
Granular activated carbon	Replaced every 5 years (initial charge nearly 3 times the minimum charge required)
Gas velocity	30.5 m/min (100 fpm)
Bed depth	0.9 m (3 ft)

Pressure drop	5,257 Pa/m (6.5 in H_2O/ft)
Carbon	4 X 10 mesh BPL carbon, 480 kg/m^3 (30 lb/ft^3)
Benzene recovery credit	$0.22/kg ($0.10/lb)
Benzene removal efficiency	99%

The cost estimates and cost effectiveness for the control of benzene and total VOC emissions from the model-plant main process vent and refining vacuum vent are shown on Table VI-1. The cost factors used to compute the annual costs are shown in Table VI-2. A sample of the calculations used in conjunction with the control device report for carbon adsorption[1] are shown in Appendix D. All cost estimates are adjusted to December 1979.

Corrosion-resistant type 316 stainless steel is required throughout the caustic scrubber. The costs of the scrubber and heater are included in the cost estimate. It is assumed that all the nonbenzene VOC is removed by the caustic scrubber pretreatment. Nearly identical capital and cost-effectiveness figures have been reported for an existing carbon adsorption system operating at 85% VOC removal efficiency.[3] These data indicate that the cost effectiveness is not appreciably less for a system operating at a lower efficiency. Costs of systems for removal efficiencies of more than 99% are not included because such higher efficiencies would be practically impossible tc obtain.

Figure VI-1 is a plot of the installed capital and net annual costs for carbon adsorption systems developed from the model-plant calculations and of costs calculated for a plant with one-half the capacity of the model plant plus a plant with a capacity that is 50% larger than that of the model plant. The calculated results for all three plant sizes are listed in Appendix D.

Incineration—Estimated costs are based on the incineration system described in Sect. V. A well-designed and operated incinerator will have a VOC removal efficiency greater than 99%. The cost savings of operating at a lower efficiency do not appear to be justified. Higher removal efficiencies might increase the cost significantly because of the disproportionately large increase in combustion temperature and residence time required. One incinerator was reported to operate at 760°C with a VOC removal efficiency of 93%.[4]

Table VI-1. Carbon Adsorption System Emission Control Cost Estimate for Model Plant (Main Process Vent and Refining Vacuum Vent)

Installed capital (excluding pretreatment)	$ 780,000
Caustic scrubber pretreatment installed capital	542,000
Total installed capital	$1,322,000
Utilities, per year	258,000
Raw materials and chemicals, per year	80,000
Manpower, per year	24,000
Capital recovery, per year	383,000
Benzene recovery credit, per year	(330,000)
Net annual cost	$415,000
Benzene emissions reduced, Mg/yr	1,500
Total VOC emissions reduced, Mg/yr	1,947
Cost effectiveness per Mg of benzene reduced	277
Cost effectiveness per Mg of total VOC reduced	213

Table VI-2. Cost Factors Used to Compute Annual Costs

Operating factor	8760 hr/yr
Operating labor	$15/hr
Maintenance labor plus materials, 6%	29% of installed capital
Capital recovery, 18% (10-yr life at 12% interest)	
Taxes, insurance, administration, 5%	
Utilities	
Electric power	$8.33/GJ ($0.03/kWh)
Steam	$5.50/Mg ($2.50/thousand lb or million Btu)
Cooling water	$0.026/m^3 ($0.10/thousand gal)
Natural gas	$1.90/GJ ($2.00/million Btu)
Heat recovery credits (equivalent to natural gas)	$1.90/GJ ($2.00/million Btu)
Activated carbon (replacement)	$2.58 kg ($1.17/lb)

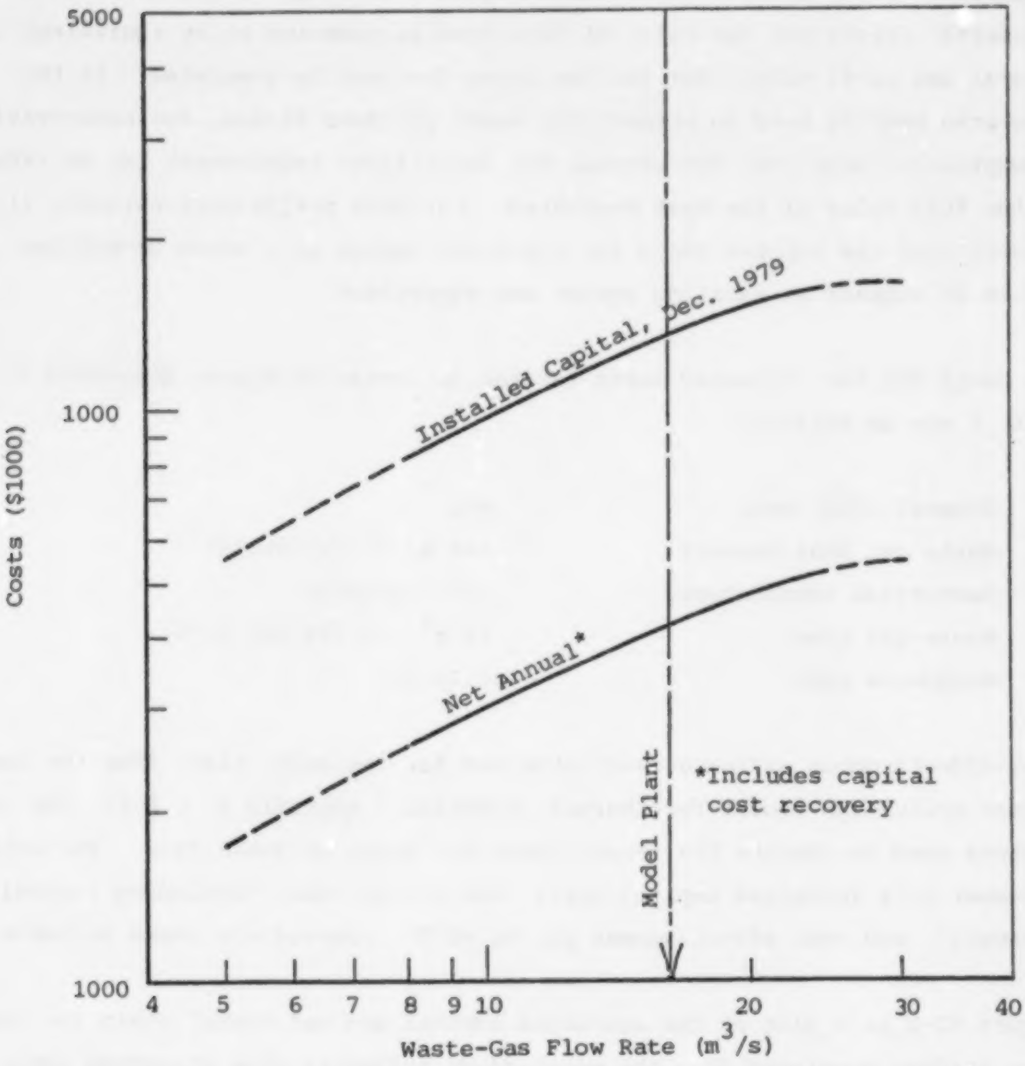

Fig. VI-1. Cost vs Waste-Gas Flow Rate - Carbon Adsorption

Heat recovery from incineration can be used to generate steam or to preheat the incinerator feed stream to reduce supplemental fuel requirements. For this comparative study it was assumed that 50% of the energy in the exit stream is recovered. Credit for the value of this heat is computed to be equivalent to natural gas at $1.90/GJ, not for the steam that may be generated. If the recovered heat is used to preheat the waste gas feed stream, the conservative assumption is made that the natural gas (utilities) requirement can be reduced by the full value of the heat recovered. For this preliminary estimate it was assumed that the capital costs for a preheat system or a steam generation system to augment an existing system are equivalent.

The basis for the estimated costs for the incineration system described in Sect. V are as follows:

Removal efficiency	99%
Waste-gas heat content	484 kJ/m^3 (13 Btu/ft^3)
Combustion temperature	871°C (1600°F)
Waste-gas flow	16 m^3/sec (34,000 scfm)
Residence time	0.75 sec

Cost-effectiveness estimates were obtained for the model plant from the control device evaluation report for thermal oxidation,[2] Appendix B, p B-18. The cost factors used to compute the annual costs are shown in Table VI-2. The estimated December 1979 installed capital costs, net annual costs (including capital recovery), and cost effectiveness per Mg of VOC removed are shown in Table VI-3.

Figure VI-2 is a plot of the installed capital and net annual costs for incineration systems developed from the model-plant estimates plus projected costs for a plant with one-half the capacity of the model plant plus a plant with a capacity that is 50% larger than that of the model plant. The costs and cost effectiveness projected for all three plant sizes are listed in Appendix D. Figure VI-3 is a plot of the same information for an incinerator system with 50% heat recovery.

Cost Effectiveness——Figure VI-4 is a plot of cost effectiveness versus capacity for each of the benzene and total VOC removal control systems considered. The data for Fig. VI-4 are listed in Tables D-1 and D-2.

Table VI-3. Incineration System Emission Control Cost Estimate for Model Plant (Main Process Vent and Refining Vacuum Vent)

	No Heat Recovery	50% Heat Recovery
Installed capital	$980,000	$1,300,000
Net annual costs (including capital recovery)	$2,200,000	$700,000
Benzene emission reduced, Mg/yr	1500	1500
Total VOC emissions reduced, Mg/yr	1943	1943
Cost effectiveness per Mg of benzene reduced	$1467	$467
Cost effectiveness per Mg of total VOC reduced	$1132	$360

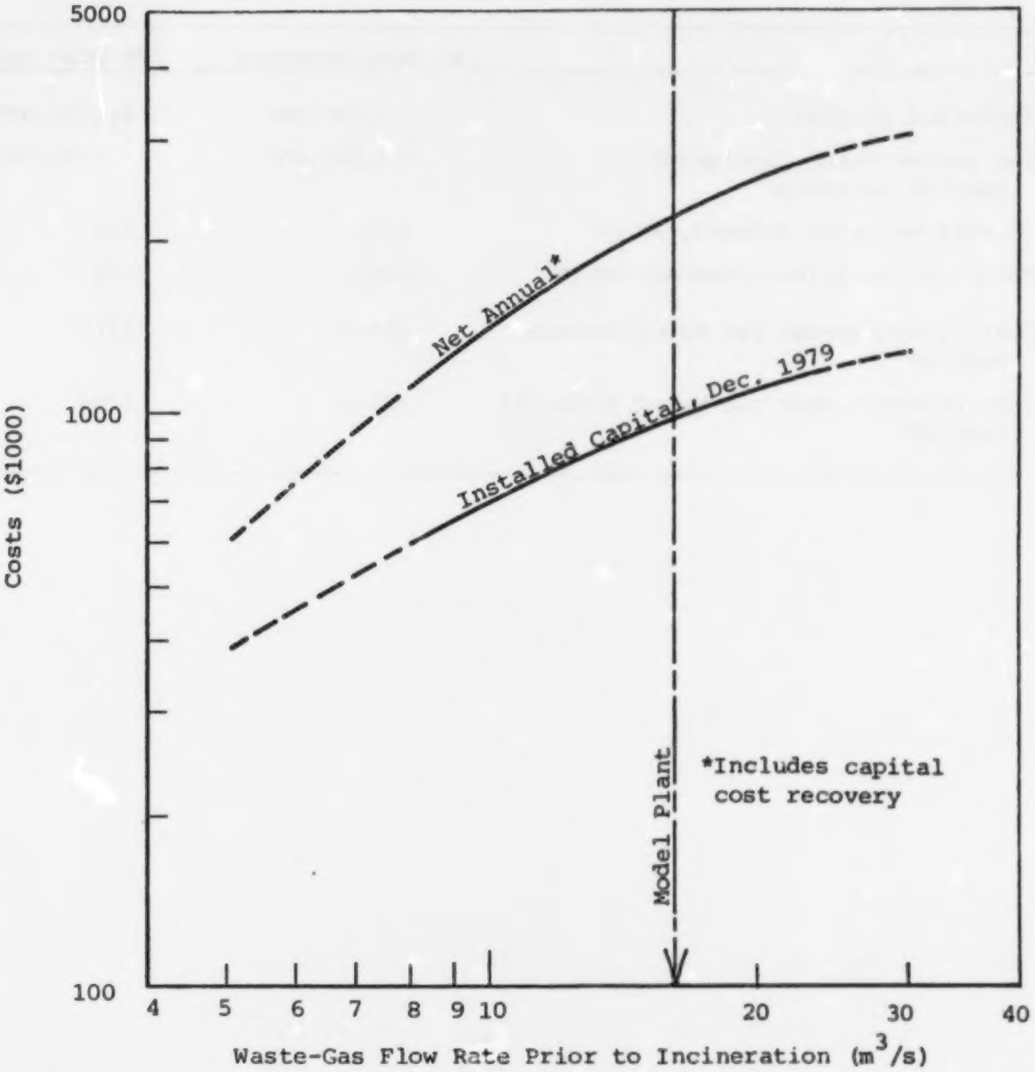

Fig. VI-2. Cost vs Waste-Gas Flow Rate - Incineration Without Heat Recovery

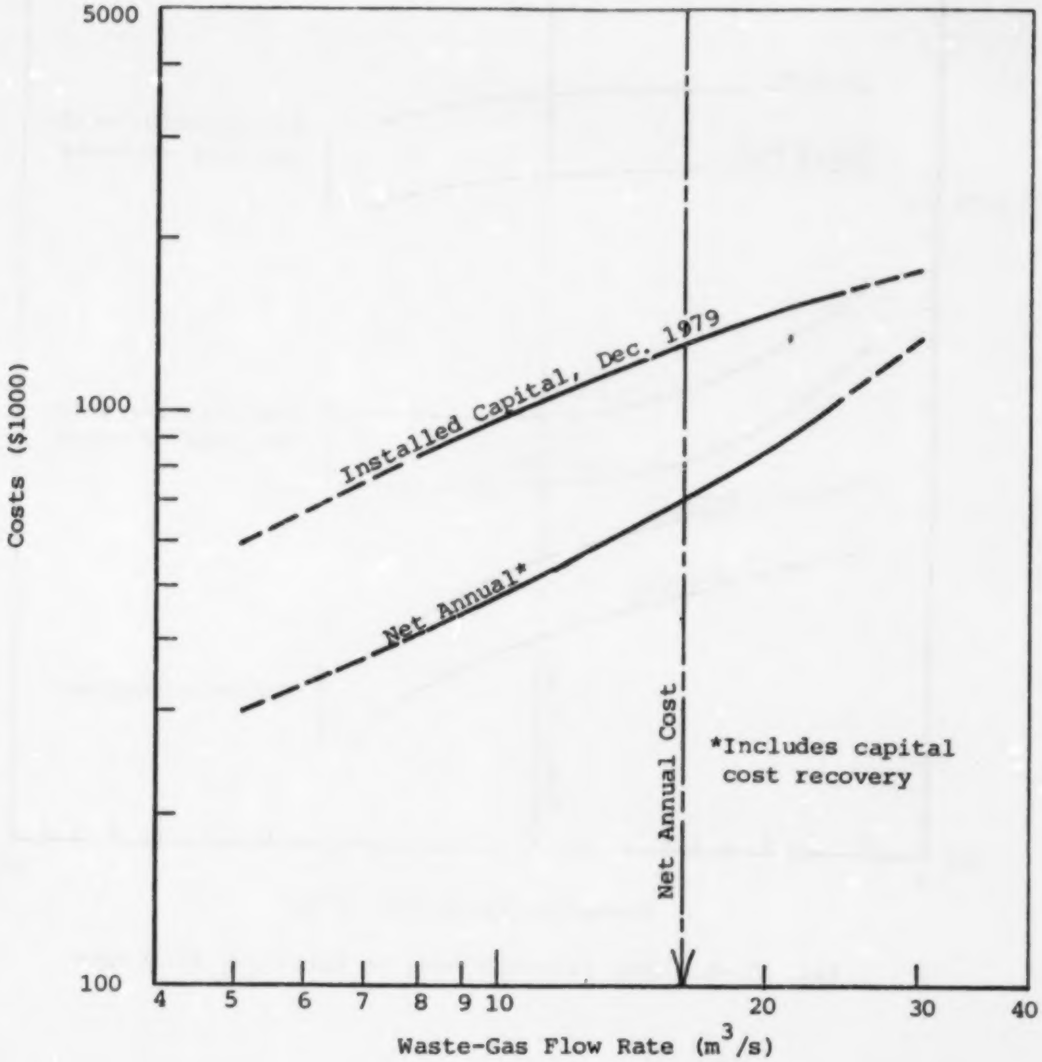

Fig. VI-3. Cost vs Waste-Gas Flow Rate - Incineration with 50% Heat Recovery

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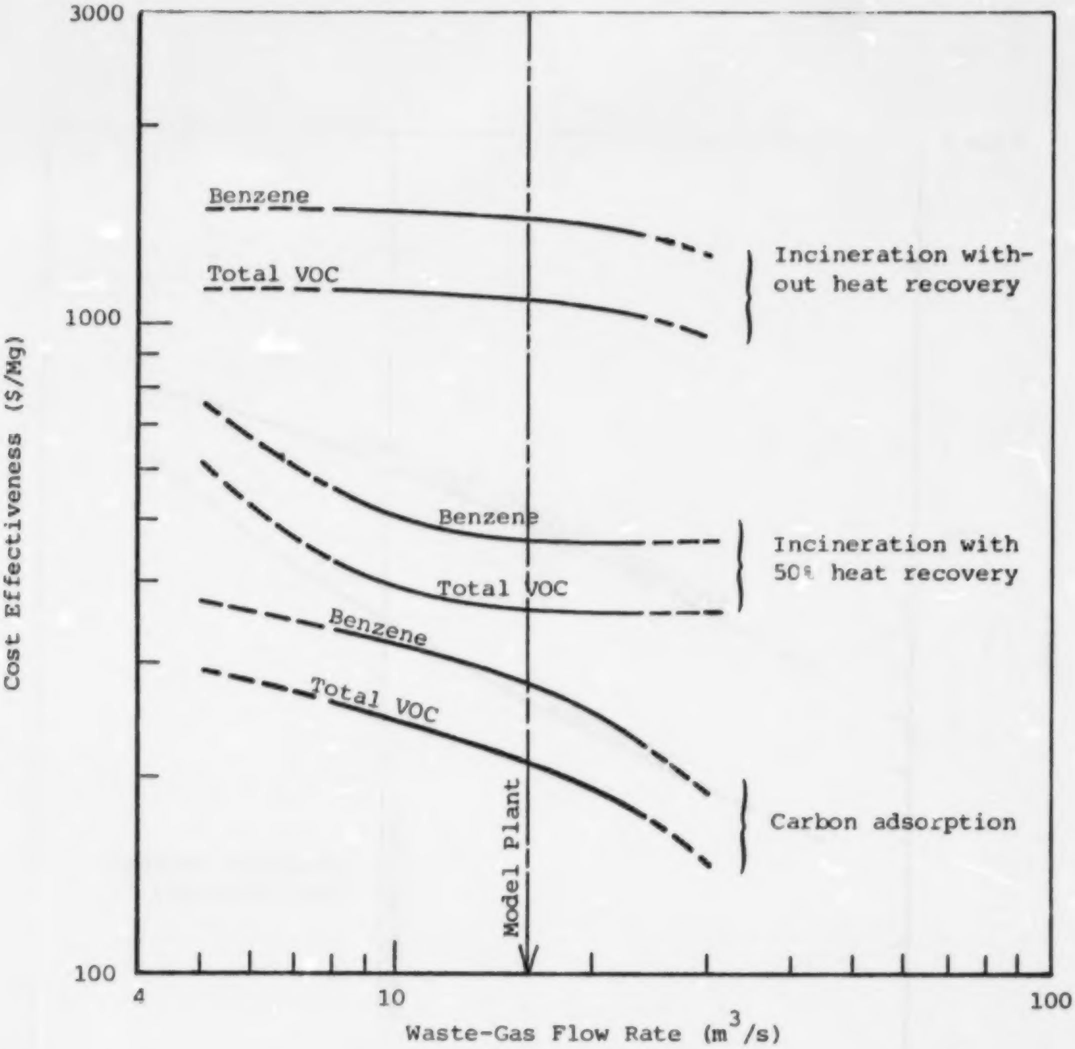

Fig. VI-4. Cost Effectiveness vs Waste-Gas Flow Rate

Fugitive Emissions——Fugitive emissions factors are listed in Appendix C. A fugitive emissions report covers the applicable fugitive emissions controls for all the synthetic organic chemicals manufacturing industry.[5]

Storage and Handling——Storage control costs and cost effectiveness are covered by a storage and handling report for the entire synthetic organic chemicals manufacturing industry.[6]

Secondary Emissions——No significant secondary emissions sources exist for the model plant; therefore no control is required.

Other Processes——No data are available for determining the cost impact of converting to the n-butane process as a benzene emission control option. Data are also unavailable for determining the cost of any control devices required to control emissions from an n-butane oxidation process.

B. ENVIRONMENTAL AND ENERGY IMPACTS

Table VI-4 shows the environmental impact of reduced benzene and VOC emissions by application of the described control systems to the model plant. From an energy standpoint a typical uncontrolled MA process will produce a heat surplus of approximately 15 kJ/kg of MA.[7] Control device environmental and energy impacts are discussed below.

1. Carbon Adsorption

The carbon adsorption system described to control process emissions from the model plant will reduce benzene emissions by 1500 Mg/yr and total VOC emissions by 1947 Mg/yr. Energy (steam) is required to condition and desorb the benzene from the carbon. For the model plant this energy (as steam) is 56,000 MJ/Mg of benzene emissions reduced and 43,000 MJ/Mg of total VOC removed. For the total domestic MA production capacity this is equivalent to 800 million MJ/yr. The benzene recovered is recycled to the process rather than being used as fuel.

The electrical energy required is 2300 MJ/Mg of benzene emissions reduced and 1700 MJ/Mg of VOC removed. For the total domestic MA production capacity this is equivalent to 33 million MJ/yr.

Table VI-4. Environmental Impact - Model Plant Emission Controlled

Emission Source	Stream	Control Device or Technique	Emission Reduction (%)	Emissions Controlled (Mg/yr)	
				Benzene	Total VOC
Main process vent	A	Carbon adsorption or	99	1500	1947[a]
Refining vacuum vent	B	Incineration	99	1500	1943
Storage					
Benzene[b]	C	Floating-roof tank	85		
MA	C	Scrubber	99	23.8	24.7
Xylene	C	None			
Fugitive[c]	J	Detection and correction of major leaks	∿65	20.9	20.6
Secondary	K	None			
				1545	1993[a] 1989

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[a] VOC removal with carbon adsorption, which is slightly higher because of the VOC removed by the caustic scrubber.

[b] Approximately 65% of the storage emissions does not vary with production rate.

[c] Fugitive emissions do not vary with production rate.

2. Incineration

The incineration system described to control process emissions from the model plant will reduce benzene emissions by 1500 Mg/yr and total VOC emissions by 1943 Mg/yr. No organics are recovered for recycle to the process with incineration. Stack gases from incineration can have a negative impact on the environment (NO_x, CO_2, CO), particularyly if the carbon monoxide is not adequately oxidized.

Supplemental fuel is required to maintain suitable operating conditions. The net amount of energy required for the model plant ranges from 666 GJ/Mg of benzene removed for an incinerator without heat recovery to 70 GJ/Mg for an incinerator with 50% heat recovery. For total VOC removal the net energy requirement ranges from 514 GJ/Mg without heat recovery to 54 GJ/Mg with 50% heat recovery. The net energy required for all domestic MA production projects ranges from 9.4 million GJ/yr without heat recovery to 1.0 million GJ/yr with 50% heat recovery. Because the potential exists for some companies to have excess steam on-site, it may not be practical for all companies to utilize the heat recovery option.

3. Other Emissions (Fugitive, Storage, and Secondary)

The control methods described for emissions from these sources are floating-roof storage tanks, scrubbing for product vents, and correction of leaks for fugitive emission control. Application of these systems results in a VOC emission reduction of 45 Mg/yr for the model plant. The energy impact resulting from application of these systems is minimal because the only energy required is electricity for pumps.

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C. REFERENCES*

1. H. S. Basdekis, IT Enviroscience, Inc., Control Device Evaluation. Carbon Adsorption (in preparation for EPA, ESED, Research Triangle Park, NC).
2. J. W. Blackburn, IT Enviroscience, Inc., Control Device Evaluation. Thermal Oxidation (July 1980) (EPA/ESED report, Research Triangle Park, NC).
3. J. F. Lawson, IT Enviroscience, Inc., Trip Report for Visit to Reichhold Chemical, Inc., Morris, IL, July 28, 1977 (data on file at EPA, ESED, Research Triangle Park,, NC).
4. Personal communication Nov. 17, 1977, between J. L. Lawson, IT Enviroscience, Inc., and R. E. Hinkson, Denka USA.
5. D. G. Erickson, IT Enviroscience, Inc., Fugitive Emissions (in preparation for EPA, ESED, Research Triangle Park, NC).
6. D. G. Erickson, IT Enviroscience, Inc., Storage and Handling (in preparation for EPA, ESED, Research Triangle Park, NC).
7. P. L. Morse, Maleic Anhydride, Interim A1, 46A1, A private report by Process Economic Program, Standford Research Institute, Menlo Park, CA (November 1973).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VII. SUMMARY

Maleic anhydride is produced in the United States predominantly by catalytic oxidation of benzene. In recent years producers have been looking very carefully at the feasibility of n-butane as a feedstock. Late in 1976 Amoco began operation of a 27,000-Mg/yr plant using butane feedstock. In 1974 Monsanto also dedicated 20% of its capacity toward development of butane technology and during 1979 announced expansion of their butane facilities. Denka USA has notified the regulatory agencies of its intent to engage in butane process development. Approximately 83% of the 214,000-Mg/yr domestic capacity is based on benzene oxidation. Butane oxidation accounts for another 15% of capacity, and the remaining 2% is produced as a by-product of phthalic anhydride manufacture.

The maleic anhydride annual growth rate is estimated to be 8% through 1982. Based on 1977 domestic MA production capacity there is sufficient capacity at present to meet the growth rate through 1982. No shortage of either benzene or n-butane is expected during this period.

The emission sources and control levels for the model plant are summarized in Table VII-1. The predominant emission points are the main process vent and benzene storage facilities. Control of these sources alone can reduce emissions by 99%.

The model-plant main process vent emits benzene at a rate of 173 kg/hr and total VOC at 224 kg/hr. These process emissions can be controlled by either carbon adsorption or incineration with a destruction efficiency of 99%. The installed capital cost to control process emissions from the model plant ranges from $980,000 for an incineration system without heat recovery to $1,300,000 for an incinerator system with heat recovery. The carbon adsorption installed capital cost is estimated to be $780,000. The net cost effectiveness per Mg of reduction is as follows:

	Benzene (per mg)	Total VOC (per mg)
Carbon adsorption	$ 277	$ 213
Incineration without heat recovery	1467	1132
Incineration with 50% heat recovery	467	360

Table VII-1. Summary of Uncontrolled and Controlled Emissions from Model Plant (22,700-Mg/yr Capacity)

	Emission Rate (kg/hr)				
	Uncontrolled		Controlled		
Emission Source	Benzene	VOC	Benzene[a]	VOC	
Process	173	224	1.73	2.24[b]	1.73[c]
Storage and handling	3.2	3.3	0.48	0.48	0.48
Fugitive	2.93	3.23	0.54	0.88	0.88
Secondary	—	0.3	—	0.3	0.3
Total	179	230	2.8	3.9	3.4

[a] Benzene controlled emissions are identical for carbon adsorption and incineration.

[b] Based on incineration option.

[c] Based on carbon adsorption; VOC emissions are lower because of the VOC removed by caustic scrubbing prior to carbon adsorption.

The carbon adsorption system requires an estimated 84 million MJ of steam energy per year for the model plant and 3 million MJ of electrical energy per year. The incineration system requires an estimated 1000 million MJ of supplemental fuel energy per year for an incineration system without heat recovery and a net requirement of 105 million MJ/yr for a system with 50% heat recovery. With either control system the vacuum vent system is tied to the control device feed and all estimates include these emissions.

Benzene storage can be controlled by use of a floating-roof tank with an emission reduction of 85% of the fixed-roof-tank emissions.

A carbon adsorption system is currently being used to recover benzene from an MA operation, but reportedly has achieved only 85% efficiency.[1] One MA producer using incineration for VOC emission control reports a removal efficiency of 93%.[2]

Since the n-butane oxidation process has no inherent benzene emissions, it is an option for benzene emission control. However, data regarding the potential economic incentive for switching to n-butane oxidation are not presently available. It's increased popularity is evidenced by the fact that a growth rate of 24.3% is projected for n-butane oxidation through 1982 compared to 8% for total maleic anhydride production.

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[1] J. F. Lawson, IT Enviroscience, Inc., Trip Report for Visit to Reichhold Chemicals, Inc., Morris, IL, July 28, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

[2] Personal communication Nov. 17, 1977, between J. F. Lawson, IT Enviroscience, Inc., and R. E. Hinkson, Denka USA.

APPENDIX A

Table A-1. Physical Properties of Maleic Anhydride[a]

Synonyms	Toxilic anhydride, cis-butene dioicanhydride, 2,5-furandione[b]
Molecular formula	$C_4H_2O_3$
Molecular weight	98.06
Physical state	Solid
Vapor pressure	1 mm at 44°C
Vapor density	3.4
Boiling point	197—199°C
Melting point	60°C
Density	1.48 at 20°C/4°C
Water solubility	Reacts with water

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[a] J. Dorigan, B. Fuller, and R. Duffy, "Maleic Anhydride," pp AIII-8 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals f-n)*, MTR-7248, Rev 1, Appendix III, MITRE Corp., McLean, VA (September 1976).

[b] *The Merck Index*, 8th ed., Merck & Co., Rahway, NJ, 1968.

Table A-2. Physical Properties of Benzene[a]

Synonyms	Benzol, phenylhydride, coal naphtha
Molecular formula	C_6H_6
Molecular weight	78.11
Physical state	Liquid
Vapor pressure	95.9 mm at 25°C
Vapor density	2.77
Boiling point	80.1°C at 760 mm
Melting point	5.5°C
Density	0.8787 at 20°C/4°C
Water solubility	Slight (1.79 g/liter)

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[a] J. Dorigan, B. Fuller, and R. Duffy, "Benzene," p AI-102 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals a-c)*, MTR-7248, Rev 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

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Table A-3. Physical Properties of Formic Acid[a]

Synonyms	Methanoic acid, hydrogen carboxylic acid
Molecular formula	CH_2O_2
Molecular weight	46.3
Physical state	Liquid
Vapor pressure	42.38 mm at 25°C
Vapor density	1.59
Boiling point	100.8°C
Melting point	8.3°C
Density	1.2201 at 20°C/4°C
Water solubility	Soluble

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[a] J. Jorigan, B. Fuller, and R. Duffy, "Formic Acid," p AIII-16 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals f-n), MTR-7248, Rev 1, Appendix III, MITRE Corp., McLean, VA (September 1976).

Table A-4. Physical Properties of Formaldehyde[a]

Synonyms	Methanol, methyl aldehyde, formalin
Molecular formula	CH_2O
Molecular weight	30.03
Physical state	Gas or liquid
Vapor pressure	1946.67 mm at 25°C
Vapor density	Not given
Boiling point	-21°C at 760 mm
Melting point	-92°C
Density	0.815 at 20°C/4°C
Water solubility	Soluble

[a] J. Dorigan, B. Fuller, and R. Duffy, "Formaldehyde," p AIII-12 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals f-n)*, MTR-7248, Rev 1, Appendix III, MITRE, Corp., McLean, VA (September 1976).

Table A-5. Physical Properties of Maleic Acid[a]

Synonyms	Maleinic acid, toxilic acid, cis-butenedioic acid
Molecular formula	$C_4H_4O_4$
Molecular weight	116.07
Physical state	Solid
Vapor pressure	Essentially zero
Vapor density	4.0
Boiling point	135°C; decomposes
Melting point	139 to 140°C
Density	1.590 at 20°C/4°C
Water solubility	Very soluble

[a] J. Dorigan, B. Fuller, and R. Duffy, "Maleic Acid," p AIII-116 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals f-n)*, MTR-7248, Rev 1, Appendix III, MITRE Corp., McLean VA (September 1976).

APPENDIX B

Table B-1. Air-Dispersion Parameters for Model Plant (22,700-Mg/yr capacity)

Source	Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temp. (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
Process emissions (uncontrolled)		27.4	1	311	20.3	25.8
Benzene	48.1					
Total VOC	61.9					
Incinerator (with heat recovery)		14.0	2	533	31.4	10.0
Benzene	0.48					
Total VOC	0.62					
Carbon adsorber		15.2	1.5	333	18.0	10.2
Benzene	0.48					
Total VOC	0.48					
Storage and handling emissions						
Uncontrolled						
Benzene	0.41	12	16	Ambient		
	0.04	6	4	Ambient		
Maleic anhydride	0.04	9	7	350		
	0.02	6	6	344		
	0.02	9	7	333		
Xylene	0.01	6	5	Ambient		
Storage and handling emissions						
Controlled						
Benzene	0.01	12	16	Ambient		
	0.01	6	4	Ambient		
Maleic anhydride[a]	Trace	9.1	0.6	298	3.34	11.8
Xylene	0.01	6	5	Ambient		
Fugitive emissions[b]						
Uncontrolled						
Benzene	0.81					
Total VOC	0.90					

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Table B-1. (Continued)

Source	Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temp. (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
Fugitive emissions (cont.)						
Controlled						
Benzene	0.15					
Total VOC	0.24					
Secondary emissions (uncontrolled) (total VOC)	0.08			Ambient		

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[a] Storage scrubber.

[b] Fugitive emissions are evenly distributed over a rectangular area 150 m by 30 m.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

DETAILED COST ESTIMATES AND CALCULATIONS FOR CARBON ADSORPTION INCINERATION

This appendix contains an explanation and sample calculations for the estimated costs used in this report.

Capital costs shown are based on an accuracy range of +30% to -23%. This range is a function of the degree of detailed data available when the estimate was made. The evaluation made in this report is a screening study based on general design criteria, block flowsheets, approximate material balances, and general equipment requirements. Figure D-1 illustrates the relationship between the degree of accuracy of an estimated cost and the amount of data available. The allowance indicated on this chart to cover the undefined scope of the project has been included in the estimated costs.

This type of estimate is an acceptable basis to provide a screening estimate to indicate the most cost-effective alternative, within the limits of accuracy indicated.

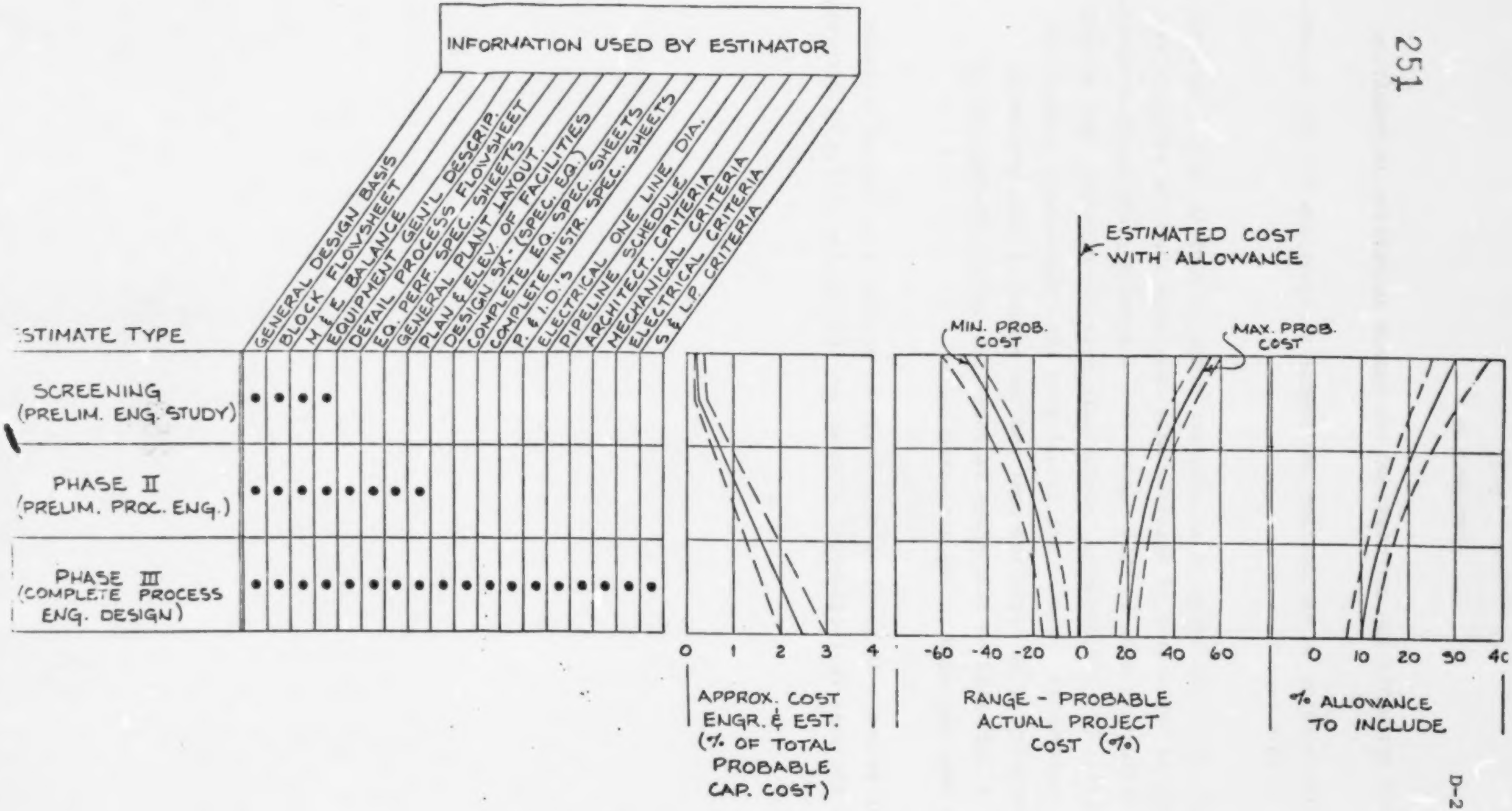

Fig. D-1. Precision of Capital Cost Estimates

A. CARBON ADSORPTION

The following procedure was used to prepare the emission control cost estimates for Table VI-1. As shown by Table IV-2 the emission stream to be controlled contains 173 kg of benzene per hour and 224 kg of total VOC per hour. Essentially all VOC except benzene will be removed by the caustic scrubber pretreatment.

1. Emissions to Carbon Adsorption (CA) System

$$\text{Benzene} = \frac{173\ \text{kg}}{\text{hr}}\ \frac{2.2\ \text{lb}}{\text{kg}}\ \frac{\text{hr}}{60\ \text{min}}\ \frac{\text{lb mole}}{78\ \text{lb}}\ \frac{359\ \text{ft}^3}{\text{lb mole}} = 29.20\ \text{scfm}$$

Air = 75,427 kg/hr = 34,236 scfm

Total waste gas to CA = 34,266 scfm

From Fig. IV-1 of Control Device Evaluation. Carbon Adsorption[1] (CA) the December 1979 installed capital cost for 34,000 scfm is $780,000, including 67,500 lb of carbon. The pretreatment caustic scrubbing system requires a stainless steel scrubber 8 ft in diameter by 36 ft high, with 402 ft^3 of saddles, a stainless steel 100-gpm circulation pump, a 500-gal sump tank, and a 900-ft^2 heat exchanger, plus instrumentation for level, pH, and temperature control. The installed capital estimate for the pretreatment system is $542,000. Total installed capital cost is $1,322,000.

2. Annual Cost

a. Utilities—The following items comprise the cost of utilities:

$$\text{Regeneration} = \frac{381\ \text{lb of benzene}}{\text{hr}}\ \frac{20\ \text{lb of steam}}{\text{lb of benzene}}\ \frac{970\ \text{Btu}}{\text{lb of steam}} \times$$

$$\times \frac{\$2.50}{\text{M Btu}}\ \frac{8760\ \text{hr}}{\text{yr}} = \$161{,}872/\text{yr}$$

Conditioning = 1,819 lb of steam/hr = $ 38,641/yr

$$\text{Blower electricity (App. A, ref 1)} = \$4{,}925 \times \frac{30{,}000}{5{,}000} = \$\ 29{,}550/\text{yr}$$

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[1] H. S. Basdekis, IT Enviroscience, Inc., Control Device Evaluation. Carbon Adsorption (in preparation for EPA, ESED, Research Triangle Park, NC).

$$\text{Cooling water} = \frac{4.2\ \text{gal}}{\text{lb of steam}}\ \frac{67\ \bar{M}\ \text{lb of steam}}{\text{yr}}\ \frac{\$0.10}{\text{M gal}} = \$\ \underline{28{,}140}$$

Total utilities $258,203

b. Raw Materials and Chemicals——The cost of raw materials and chemicals includes carbon replacement and caustic:

$$\text{Carbon replacement} = \frac{22{,}500\ \text{lb}}{\text{bed}}\ \frac{3\ \text{beds}}{5\ \text{yr}}\ \frac{\$1.17}{\text{lb}} = \$\ 15{,}795$$

$$\text{Caustic} = \frac{82\ \text{lb}}{\text{hr}}\ \frac{8760\ \text{hr}}{\text{yr}}\ \frac{\$0.09}{\text{lb}} = \underline{\$\ 64{,}649}$$

Total $ 80,444

c. Manpower—— 1600 hr/yr X $15/hr = $ 24,000

d. Fixed Cost (Including Capital Recovery)—— 0.29 X $1,322,000 = $383,380

e. Benzene Recovery Credit——

$$\frac{381\ \text{lb of benzene}}{\text{hr}}\ \frac{8760\ \text{hr}}{\text{yr}} \times$$

$$\times\ 0.99\ \frac{\$0.10}{\text{lb of benzene}} = (\underline{\$330{,}418})$$

Net annual cost $415,609*

3. Cost Effectiveness

a. Benzene Emissions Reduced (Table IV-2)——173 kg/hr X 8760 hr/yr X X 0.99 X 1/1000 = 1500 Mg/yr

b. Total VOC Reduced——

$$\frac{5\ \text{kg/hr} \times 8760\ \text{hr/yr}}{1000} + 1500\ \text{Mg/yr} = 1947\ \text{Mg/yr}$$

c. Cost Effectiveness of Benzene——$415,609/1500 Mg = $277/Mg

d. Cost Effectiveness of VOC——$415,609/1947 Mg = $213/Mg

Table D-1 lists the carbon adsorption control cost estimates for the model plant plus plants with 50% greater and lesser capacity.

B. INCINERATION

The following procedure was used to prepare the estimated cost projections for Table VI-3 plus those in Figs. VI-2 and VI-3.

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*After the annual cost is adjusted for pretreatment capital recovery cost, caustic cost, and steam conditioning cost, the net annual cost is in agreement with that of Figs. IV-4 and IV-5 of the carbon adsorption report.

Table D-1. Carbon Adsorption System Emission Control Costs for Main Process Vent and Refining Vacuum Vent

Costs									Emission Reduction (Mg/yr)		Cost Effectiveness (per Mg)	
Installed Capital[a]	Caustic Scrubber Installed	Total Installed	Utilities	Raw Materials and Chemicals	Manpower	Fixed[b]	Benzene Recovery Credit	Net Annual	Benzene	Total VOC	Benzene	Total VOC
					17,000-scfm (8 m^3/s) Plant							
$480,000	$332,000	$ 812,000	$129,100	$ 40,221	$15,000	$235,480	($165,203)	$254,598	750	974	$339	$261
					34,000-scfm (16 m^3/s) Model Plant							
$780,000	$542,000	$1,322,000	$258,203	$ 80,444	$24,000	$383,000	($330,418)	$415,609	1500	1947	$277	$213
					51,000-scfm (24 m^3/s) Plant							
$970,000	$641,000	$1,611,000	$387,304	$120,666	$29,000	$467,190	($495,632)	$508,528	2250	2921	$226	$174

[a] Excluding pretreatment.

[b] Including capital recovery.

Waste gas Btu content (model-plant data from Table IV-2):

$$\text{CO} = \frac{1{,}761\ \text{kg}}{\text{hr}}\ \frac{2.2\ \text{lb}}{\text{kg}}\ \frac{\text{hr}}{60\ \text{min}}\ \frac{4{,}200\ \text{Btu}}{\text{lb}} = 271{,}200\ \text{Btu/min}$$

$$\text{VOC} = \frac{224\ \text{kg}}{\text{hr}}\ \frac{2.2\ \text{lb}}{\text{kg}}\ \frac{\text{hr}}{60\ \text{min}}\ \frac{18{,}000\ \text{Btu}}{\text{lb}} = \underline{147{,}840}\ \text{Btu/min}$$

$$419{,}040\ \text{Btu/min}$$

$$\frac{419{,}040\ \text{Btu}}{\text{min}}\ \frac{\text{min}}{34{,}266\ \text{scf}} = 12.1\ \text{Btu/scf}$$

The procedure used for designing thermal oxidizer systems is described on p III-7 of the control device evaluation report for thermal oxidation.[2] As is discussed on p III-7 and indicated on Fig. III-3 of that report, all tables in Appendix B of the report are based on the premise that the waste-gas contains no oxygen for combustion and that with the waste-gas Btu contents below 80 Btu/scf the volume of combustion air required is approximately equal to the volume of waste gas. Since the waste gas from a maleic anhydride process contains more than enough oxygen required for combustion, no additional combustion air is required. The cost estimates were projected by using the tables on p B-18 of the thermal oxidation report and using the costs listed for a waste-gas flow of one-half the specified flow. The tables on p B-18 apply for all waste gases with a combustion temperatures of 1600°F, a residence time of approximately 0.75 sec, and a Btu content of approximately 13 per scf. Table D-2 lists the cost estimates for the model plant plus those for plants with 50% greater and lesser capacity.

The costs of incineration utilities are attributed essentially to natural gas used as supplemental fuel. The supplemental fuel requirements discussed in Sect. VI were also obtained from Table B-18 discussed above. The supplemental fuel requirement was obtained by transposing the annual utility cost to GJ of natural gas by using the $1.90/GJ factor from Table VI-2.

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[2] J. W. Blackburn, IT Enviroscience, Inc., Control Device Evaluation. Thermal Oxidation (July 1980) (EPA/ESED report, Research Triangle Park, NC).

Table D-2. Incineration System Emission Control Costs for Main Process Vent and Refining Vacuum Vent

Plant	Cost		Emission Reduction (Mg/yr)		Cost Effectiveness (per Mg)		Cost Effectiveness (per scfm)
	Installed	Net Annual[a]	Benzene	Total VOC	Benzene	Total VOC	
34,000-scfm (16 m^3/s) model plant							
No heat recovery	$ 980,000	$2,200,000	1500	1943	$1467	$1132	$64.7
50% heat recovery	1,300,000	700,000	1500	1943	467	360	20.5
17,000-scfm (8 m^3/s) plant							
No heat recovery	$ 600,000	$1,100,000	750	971	$1467	$1130	$64.7
50% heat recovery	830,000	420,000	750	971	560	432	24.7
51,000-scfm (24 m^3/s) plant							
No heat recovery	$1,200,000	$2,800,000	2250	2914	$1244	$ 961	$54.9
50% heat recovery	1,600,000	1,600,000	2250	2914	466	360	20.6

[a] Includes capital recovery.

APPENDIX E

EXISTING PLANT CONSIDERATIONS

Table E-1[1] lists process control devices reported to be in use by industry. To gather information for the preparation of this report four site visits were made to manufacturers of maleic anhydride. Trip reports have been cleared by the companies concerned and are on file at EPA, ESED, in Research Triangle Park, NC.[2—5] Some of the pertinent information concerning process emissions from these existing maleic anhydride plants is presented in this appendix.

A. PROCESS EMISSIONS FROM EXISTING PLANTS

1. Reichhold Chemicals, Morris, IL

The process was licensed from Lurgi and the plant was built by Badger in 1971. Variations between the Lurgi process and the model process are the following: a series of switch condensers serve as primary recovery in lieu of crude-product separators; a carbon adsorption system recovers benzene from the secondary-product-recovery absorber; double-effect evaporators are used to dehydrate the maliec acid formed during secondary product recovery; and a thermal oxidizer is used to incinerate the process organic effluents. The total annual cost for operating all pollution control facilities is $865,000 (1976 dollars).

The carbon adsorption system cycle consists of 2 hr on line and 1 hr of steam regeneration. The process gas is then vented to the atmosphere. During regeneration the benzene-water vapor is condensed and separated. The benzene layer is recycled to the process, and the water layer is pumped to the process thermal oxidizer for use as quench water.

The vacuum system from the dehydration and purification sections is vented to the atmosphere. The vacuum systems are two-stage jets with barometric condensers. The water discharge is used for lean-acid scrubber makeup. No vent emission data are available.

Some key operating parameters associated with the operation of the carbon adsorption benzene recovery system are as follows:

Table E-1. Control Devices Currently Used by the Maleic Anhydride Industry in the United States

Company	Emission Point			
	Flaking, Pelletizing and Packaging	Product Recovery Absorber	Vacuum System Vent	Storage Tank Vents
Amoco Chemicals Corp.	NR	NR	NR[a]	NR
Ashland Oil, Inc.	b	Scrubber	NR	Floating-roof tanks
Denka Chemical Corp.	Scrubber	Incineration	Scrubber	Floating-roof tanks
Koppers Company, Inc.	Scrubber	Incineration	NR	Return vents
Monsanto Co.	Scrubber	c	b	Scrubber
Reichhold Chemical, Inc.				
Elizabeth, NJ	Scrubber	Carbon adsorber	NR	Conservation vents
Morris, IL	b	Carbon adsorber	c	Scrubber, conservation vents
Tenneco, Inc.	c	c	NR	Scrubber, conservation vents
U.S. Steel Corp.	Scrubber	Catalytic incinerator	NR	Floating-roof tanks

[a] Not reported.

[b] Vents to product recovery absorber.

[c] No control.

Vapor flow rate, cfm	43,000 at 100°F
Inlet temperature, °C	43 to 46
Efficiency, %	Approximately 85
Efficiency range, %	65 to 95
Adsorber vent composition, lb/hr	
Maleic anhydride	15
Benzene	18
Oxygen	31,200
Nitrogen	147,300
Carbon dioxide	7040
Carbon monoxide	3360
Water vapor	4800
Aqueous layer composition from condenser separator	
Flow, gpm	20 to 22
Benzene concentration, ppm	2 to 800
Formaldehyde concentration, %	0.3 to 0.6

The above information was extracted from a trip report.[2]

From a secondary emissions standpoint there may be some need for concern regarding the benzene concentration in the water layer being pumped to the thermal oxidizer for use as quench water. This water could conceivably average approximately 400-ppm benzene, which would essentially all be stripped from the quench water and be emitted with the thermal oxidation flue gas.

It is IT Enviroscience's belief that the most logical step to take for improvement of the 85% efficiency being experienced with the carbon adsorption system would be to further cool the bed before it is put on-line. This would require the addition of a cooling fan. Further improvement might require an additional carbon bed. The cost or practicality of this retrofit improvement has not been studied.

2. Monsanto, St. Louis, MO[3]

Variations between the Monsanto air-oxidation process and the model process are the following: the dehydration column operates at atmospheric pressure rather than under a vacuum; the xylene stripper is eliminated; and the fractionation

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column vacuum jet goes to a vent scrubber. The process emission sources are the product scrubber vent and the dehydrator decantor. The product scrubber has no control device for emission reduction. The dehydrator, which operates at atmospheric pressure, has a decanter. The decanter separates xylene and water and has a nitrogen purge of 100 scfh. The dehydrator decanter is reported to emit 0.00005 lb of xylene/lb of maleic anhydride produced. The emissions from the product scrubber are reported as follows:

Emission	Amount (lb/lb of MA Produced)
Benzene	0.062—0.104
Xylene	Trace
CO	0.548—0.564
MA	Trace

3. Denka Chemical Corp., Houston, TX[4]

The maleic anhydride production facility is essentially in agreement with the model plant. It consists of a single train with multiple reactors in parallel. The facility was built in 1962, with a major expansion in 1971. The emissions from the dehydration, stripping, and fractionation systems are vented through steam jets. The steam jets have surface-type condensers. The main process emission is the product absorber off-gas, which is incinerated.

The incinerator normally operates at 1400°F with a residence time of 0.7 sec. Hydrocarbon emissions are reportedly reduced by 91% at 1350°F and by 96% at 1500°F. Denka calculates the benzene level in the incinerator feed to be 0.001 to 0.0025 wt %. Information on benzene destruction is not available. Denka reports that their present fume incinerator cannot be operated at higher temperatures to improve VOC distruction efficiency.[6]

6. Amoco Corp., Chicago, IL[5]

The discussion of Amoco's butane-oxidation process at Joliet, IL, was held in their Chicago office without a tour of the facility. The butane-oxidation process is reportedly very similar to the benzene-oxidation process from an emissions standpoint. The one major distinction of the butane-oxidation process is that, since no benzene is present, there are no benzene emissions. The facility consists of a single train with multiple parallel reactors. The plant was built in 1976.

Product recovery is by partial condensation, product absorption, and fractionation. The combined process emissions are treated in a thermal oxidizer. Amoco test analyses of the waste gas to the thermal oxidizer and flue gas from the thermal oxidizer at 60—65% of production capacity are as follows:

Component	Waste Gas Feed (lb/hr)	Flue Gas (lb/hr)
N_2	139,000	139,000
O_2	37,000	31,500
Water	4,300	6,400
Carbon oxides	2,800	7,500
Organics	1,300	No data

The thermal oxidizer operates at 1500°F.

5. Ashland Chemical Co.[7]

No site visit was made to Ashland's maleic anhydride plant at Neal, WV. In a letter submitted by Ashland as a review of the report Ashland stated that the benzene conversion efficiency of 93.3% displayed for the model plant is well below that which is achieved at Ashland. They point out that performance of all existing plants will be upgraded as catalyst development proceeds. They suggest that 2 to 3% unconverted benzene is a better basis for emissions estimates. Ashland also contends that, with the lower estimate for benzene emissions, catalytic incineration is an appropriate method of control.

B. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

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C. REFERENCES*

1. W. A. Lewis, Jr., G. M. Rinaldi, and T. W. Hughes, Monsanto Research Corp., Source Assessment: Maleic Anhydride Manufacture (received January 1978).

2. J. F. Lawson, IT Enviroscience, Inc., Trip Report for Visit to Reichhold Chemicals, Inc., Morris, IL, July 29, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. J. F. Lawson, IT Enviroscience, Inc., Trip Report for Visit to Monsanto Industrial Chemicals Company, St. Louis, MO, Oct. 20, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

4. J. F. Lawson, IT Enviroscience, Inc., Trip Report for Visit to Denka Chemical Corporation, Houston, TX, November 17, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

5. J. F. Lawson, IT Enviroscience, Inc., Trip Report for Visit to Amoco Chemicals Corporation, Jan. 24, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

6. R. E. Hinkson, Denka Corporation, letter dated Apr. 18, 1978, to D. R. Patrick, EPA.

7. R. C. Sterritt, Ashland Chemical Company, letter dated Apr. 21, 1978, to D. R. Patrick, EPA.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 5

ETHYLBENZENE AND STYRENE

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^1
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^2
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^4
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^1
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^9	1 Gg = 1 X 10^9 grams
M	mega	10^6	1 Mg = 1 X 10^6 grams
k	kilo	10^3	1 km = 1 X 10^3 meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Ethylbenzene and styrene were selected for in-depth study because preliminary estimates indicated that their production causes relatively high volatile organic compound (VOC) emissions. These emissions include significant quantities of benzene, which was listed as a hazardous pollutant by the EPA in the Federal Register on June 8, 1977. Ethylbenzene and styrene were combined for consideration because ethylbenzene is produced almost exclusively as an intermediate for styrene production.

Benzene, ethylbenzene, and styrene are liquids at ambient conditions (see Appendix A for pertinent physical properties).

B. USAGE AND GROWTH

Since more than 99% of the ethylbenzene produced is used as an intermediate for styrene production,[1] the growth of styrene production is the dominant consideration for this report. Table II-1 shows styrene end uses, percentages of production, and expected growth rates. Virtually all styrene is consumed in polymer manufacture,[2] with more than half used to manufacture polystyrenes.[1] Packaging applications account for more than one-third of the polystyrene consumed; other diversified end uses are toys, sporting goods, appliances and cabinets, housewares, electrical parts, and disposable serviceware and flatware.[2]

The current domestic ethylbenzene capacity is 5,070,000 Mg/yr,[1—3] with the 1976 production being 55% of this capacity.[4] Production will be 78% of current capacity by 1982, based on a projected 6% annual growth in ethylbenzene consumption.[2]

The current domestic styrene capacity is 3,986,000 Mg/yr,[5] with the 1976 production being about 72% of this capacity.[6] Production levels will be nearly equal to current capacity by 1982, based on a projected 6% annual growth in styrene production.[2]

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Table II-1. Styrene Usage and Growth[a]

End Use	Percentage of Production (1976)	Average Annual Growth (%) (1976—1980)
Polystyrene	54	7
Styrene copolymer resins	17	7
Styrene-butadiene elastomers	9	2.5
Unsaturated polyester resins	6	9
Miscellaneous	1	12.5
Exports	13	-25

[a] See refs 1 and 2.

C. DOMESTIC PRODUCERS

At the end of 1977 there were 15 producers operating 18 ethylbenzene plants and 12 producers operating 14 styrene plants in the United States. Tables II-2[1,5,7–9] and II-3 list the producers, locations, capacities, and processes; Figs. II-1 and II-2 show the plant locations. Approximately 95% of the ethylbenzene capacity is based on benzene alkylation, with the remainder based on extraction of mixed xylene streams.[1] About 89% of the styrene capacity is based on ethylbenzene dehydrogenation. The remaining capacity is based on ethylbenzene oxidation followed by hydroperoxidation of propylene and dehydration to styrene.[5] The latter process was brought on-stream by Oxirane Chemical Company in 1977 and yields propylene oxide as a co-product.[7]

The companies that produce ethylbenzene/styrene are listed below:

1. American Hoechst Corporation
   Benzene is purchased for alkylation to ethylbenzene,[1] which is captively consumed in styrene manufacture.[3] The styrene is 50% captively consumed for polystyrene production.[2]

2. Cosden Oil and Chemical Company
   Ethylbenzene is separated from mixed xylenes, but additional feed must be purchased to operate the styrene plant at capacity.[1] All styrene produced is captively consumed in polystrene production.[2,3]

3. Atlantic Richfield Company
   Ethylbenzene is separated from mixed xylenes at Houston, TX, and produced by benzene alkylation at Port Arthur, TX.[1] Ethylbenzene supplies are transferred to Kobuta, PA where polystyrene and styrene-butadiene co-polymers are manufactured.[2,3]

4. Charter Company
   Ethylbenzene is separated from mixed xylenes and sold.[1,3]

5. Commonwealth Oil Refining Company, Inc.
   Ethylbenzene is separated from mixed xylenes and sold.[1,3]

Table II-2. Ethylbenzene Capacity[a]

Producer	Location	1977 Capacity (10^3 Mg)	Process
American Hoechst Corp.	Baton Rouge, LA	526	b
Cosden Oil and Chemical Co.	Big Spring, TX	47	c
Atlantic Richfield Co.	Houston, TX	50	c
	Port Arthur, TX	227	b
Charter Co.	Houston, TX	18	c
Commonwealth Oil Refining Co., Inc.	Penuelas, PR	73	c
Cos-Mar, Inc.	Carville, LA	689	b
Dow Chemical USA	Freeport, TX	782	b
	Midland, MI	249	b
El Paso Natural Gas Co.	Odessa, TX	125	b
Gulf Oil Corp.[d]	St. James, LA	313	b
Monsanto Co.[e]	Alvin, TX	23	b
	Texas City, TX	771	b,c
Oxirane Chemical Co.	Channelview, TX	526	b
Standard Oil Co.	Texas City, TX	447	b
Sun Oil Co.	Corpus Christi, TX	61	b,c
Tenneco	Chalmette, LA	16	c
Union Carbide Corp.	Seadrift, TX	154	b
Total		5097	

[a] See refs 1,5,7,8 and 10.

[b] Benzene alkylation.

[c] Mixed xylene stream recovery.

[d] Assumes that Gulf increased capacity as planned in the latter part of 1977.

[e] Not listed in all refs.

Table II-3. Styrene Capacity[a]

Producer	Location	1977 Capacity (10^3 Mg)	Process
American Hoechst Corp.[b]	Baton Rouge, LA	408	c
Cosden Oil and Chemical Corp.	Big Springs, TX	50	c
Atlantic Richfield Co.	Houston, TX	54	c
	Kobuta, PA	100	c
Cos-Mar, Inc.	Carville, LA	590	c
Dow Chemical USA	Freeport, TX	680	c
	Midland, MI	181	c
El Paso Natural Gas Co.[d]	Odessa, TX	68	c
Gulf Oil Corp.[e]	St. James, LA	272	c
Monsanto Co.	Texas City, TX	590	c
Oxirane Chemical Co.	Channelview, TX	454	f
Standard Oil Co.	Texas City, TX	363	c
Sun Oil Co.	Corpus Christi, TX	36	c
Union Carbide Corp.	Seadrift, TX	136	c
Total		3982	

[a] See refs 5 and 10.

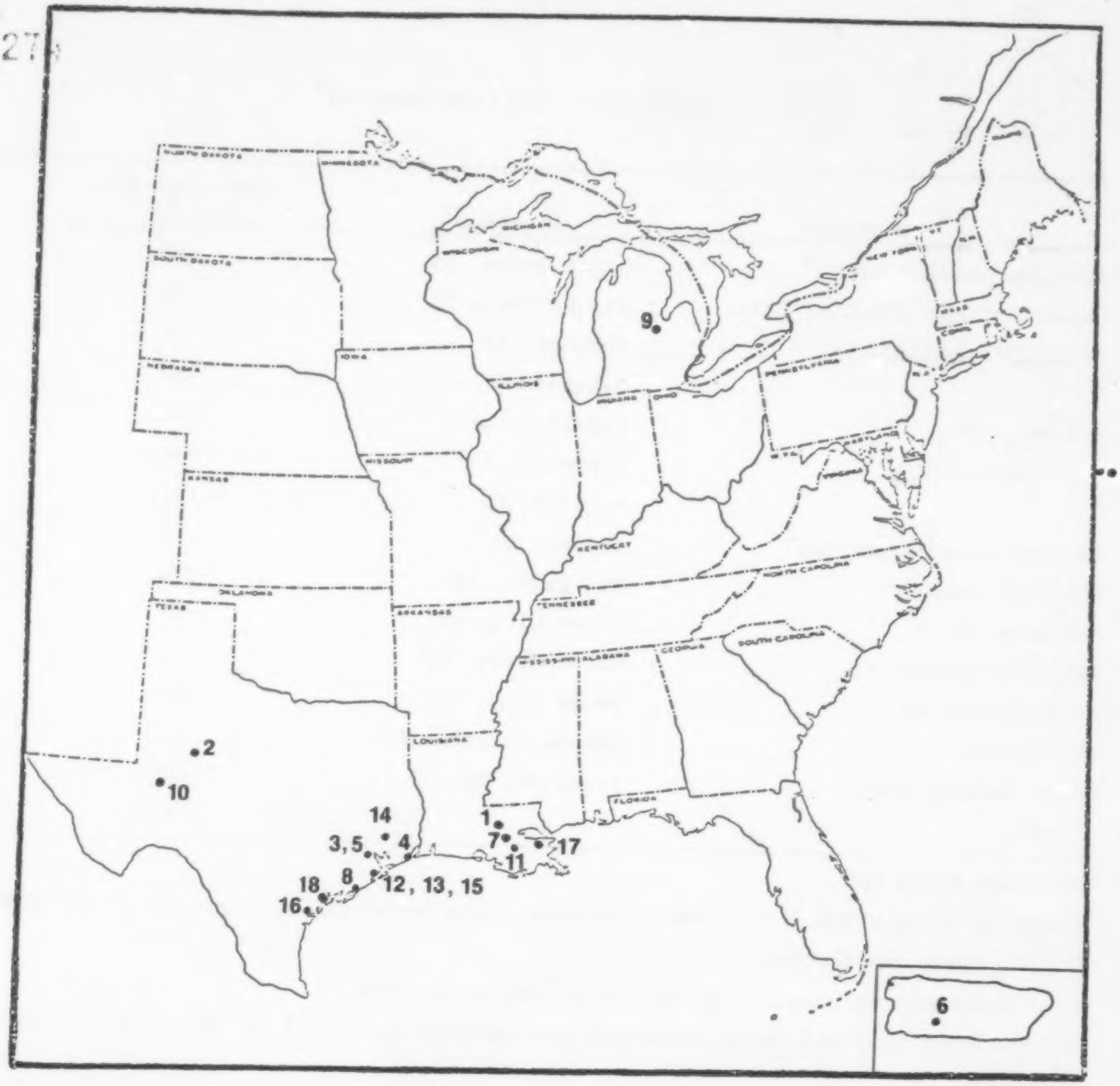
[b] Plans to bring a 408.2 X 10^3-Mg/yr styrene plant on-stream at Bayport, TX, in 1980.

[c] Ethylbenzene dehydrogenation.

[d] Will increase its capacity by 40.8 X 10^3 Mg/yr in 1978.

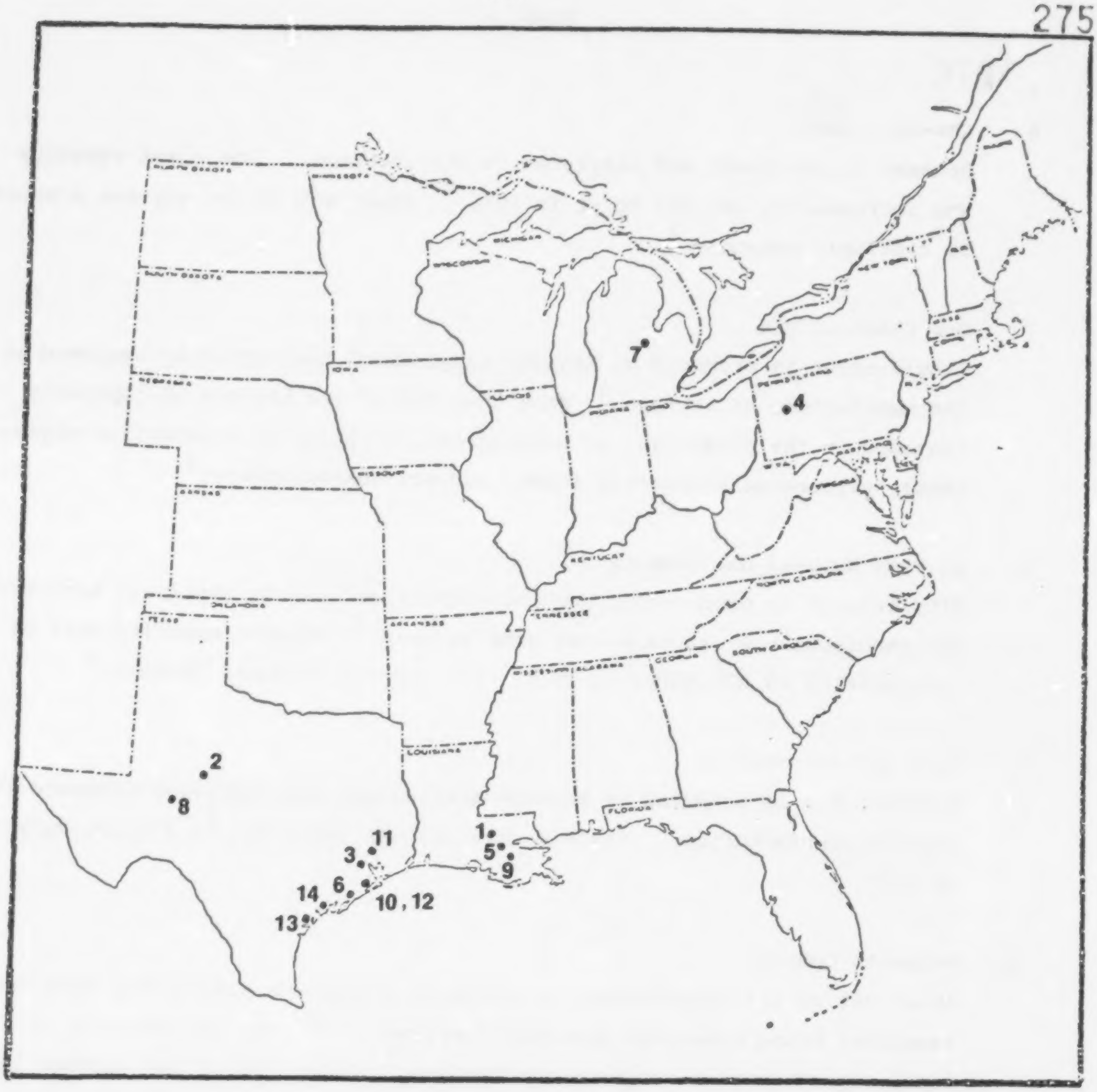
[e] Assumes that Gulf Oil Corp. increased its capacity by 34.0 X 10^3 Mg/yr in the latter part of 1977.

[f] Hydroperoxidation of propylene.



1. American Hoechst, Baton Rouge, LA
2. Cosden Oil and Chemical, Big Spring, TX
3. Atlantic Richfield, Houston, TX
4. Atlantic Richfield, Port Arthur, TX
5. Charter, Houston, TX
6. Commonwealth Oil, Penuelas, PR
7. Cos-Mar, Carville, LA
8. Dow, Freeport, TX
9. Dow, Midland, MI
10. El Paso National Gas, Odessa, TX
11. Gulf, Donaldsonville, LA
12. Monsanto, Alvin, TX
13. Monsanto, Texas City, TX
14. Oxirane, Channelview, TX
15. Standard Oil, Texas City, TX
16. Sun Oil, Corpus Christi, TX
17. Tenneco, Chalmette, LA
18. Union Carbide, Seadrift, TX

Fig. II-1. Locations of Plants Manufacturing Ethylbenzene



1. American Hoechst, Baton Rouge, LA
2. Cosden Oil and Chemical, Big Spring, TX
3. Atlantic Richfield, Houston, TX
4. Atlantic Richfield, Kobuta, PA
5. Cos-Mar, Carville, LA
6. Dow, Freeport, TX
7. Dow, Midland, MI
8. El Paso National Gas, Odessa, TX
9. Gulf, Donaldsonville, TX
10. Monsanto, Texas City, TX
11. Oxirane, Channelview, TX
12. Standard Oil, Texas City, TX
13. Sun Oil, Corpus Christi, TX
14. Union Carbide, Seadrift, TX

Fig. II-2. Locations of Plants Manufacturing Styrene

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6. Cos-Mar, Inc.

Benzene is purchased and alkylated to ethylbenzene.[1] The plant capacity was increased by 362,800 Mg/yr in 1976.[3] About 45% of the styrene produced is captively consumed.[2]

7. Dow Chemical USA

Ethylbenzene is produced by benzene alkylation[1] and captively consumed in the manufacture of styrene.[3] More than 96% of the styrene is captively consumed in the production of polystyrene, acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN), and styrene-butadiene.[2]

8. El Paso Natural Gas Company

Ethylbenzene is produced by benzene alkylation[1] and is captively consumed for manufacture of styrene, but some is sold.[3] Styrene capacity will be increased by 40,800 Mg/yr in 1978. All styrene produced is sold.[2]

9. Gulf Oil Corporation

Ethylbenzene is produced by benzene alkylation[1] and captively consumed in styrene manufacturing.[3] Styrene capacity was increased to 272,100 Mg/yr in 1977.[1]

10. Monsanto Company

About 96% of the ethylbenzene is produced by benzene alkylation, with the remainder being extracted from mixed xylenes.[1,10] All ethylbenzene is captively consumed in styrene manufacture.[3] About 35% of the styrene is captively consumed in polystyrene, ABS, and SAN production.[2]

11. Oxirane Chemical Company

Ethylbenzene is produced by benzene alkylation[1] and is captively consumed in the manufacture of styrene.[3] All styrene produced is sold.[2]

12. Standard Oil Company

Ethylbenzene is produced by benzene alkylation[1] and is captively consumed in styrene manufacture.[3] Polystyrene manufacture captively consumes 40% of the styrene.[2]

13. Sun Oil Company

Benzene alkylation produces about 65% of the ethylbenzene, with the remainder being extracted from mixed xylenes. Ethylbenzene is consumed captively in styrene manufacture.[3] All styrene produced is sold.[2]

14. Tenneco, Inc.

Ethylbenzene is extracted from mixed xylenes and sold.[1,3]

15. Union Carbide Corporation

Ethylbenzene is produced by benzene alkylation[1] and is captively consumed in styrene manufacture.[3] The company manufactures polystyrene and SAN resins from the styrene.[2]

D. REFERENCES*

1. T. C. Gunn and K. L. Ring, "Benzene," pp 618.5022 V—Y in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (May 1977).
2. S. L. Sober, "Styrene," pp 694.3052 A,B in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (January 1977).
3. S. K. Paul and S. L. Soder, "Ethylbenzene——Salient Statistics," pp 645.3000 A—H in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (January 1977).
4. "Manual of Current Indicators——Supplement Data," p 211 in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (December 1977).
5. C. V. Sleeth, "Styrene Monomer," Chemical and Engineering Progress. **73**(11), 31—35 (1977).
6. "Manual of Current Indicators——Supplement Data," p 235 in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (December 1977).
7. J. L. Blackford, "Propylene Oxide," p 690.8022 C in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (November 1976).
8. "Ethylbenzene," Chemical Marketing Reporter, p 9 (July 1, 1975).
9. T. M. Nairn, Cosden Oil and Chemical Co., letter dated June 30, 1978, to EPA.
10. H. M. Walker, Monsanto Company, Chocolate Bayou Plant, Alvin, TX, Texas Air Control Board 1975 Emissions Inventory Questionnaire, July 9, 1976.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

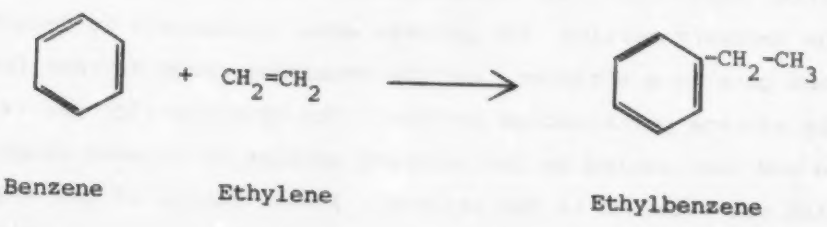
More than 95% of domestic ethylbenzene production is by benzene alkylation with ethylene. The remainder is recovered by distillation from mixed xylene streams that result from naphtha re-forming or cracking in petroleum refineries. Refinery recovery processes, however, are not within the scope of this study. More than 99% of the ethylbenzene produced is used as an intermediate for making styrene, often in an integrated ethylbenzene-styrene plant.[1] Except for a new plant brought on-stream in July 1977 by Oxirane Corporation, all domestic styrene is produced by catalytic dehydrogenation of ethylbenzene. The Oxirane ethylbenzene oxidation process is also used in Spain and Japan; however, most foreign styrene production is by dehydrogenation of ethylbenzene.[2] Future new plants will use either the conventional ethylbenzene dehydrogenation process or the Oxirane ethylbenzene oxidation process, depending on the economics of both styrene and the propylene oxide that is co-produced with styrene in the Oxirane process.[3]

B. STYRENE FROM BENZENE AND ETHYLENE

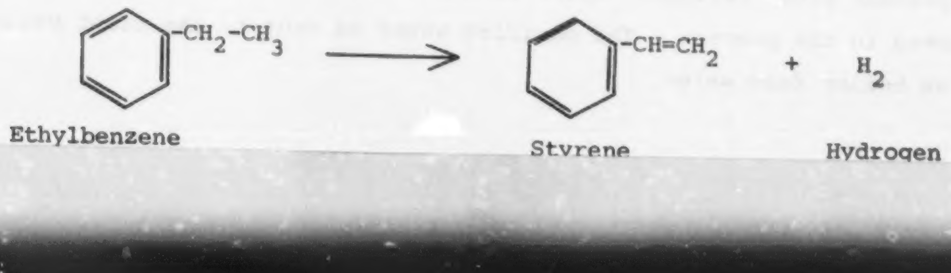
1. Basic Process [4,5]

The primary reactions in the production of styrene are catalytic alkylation of benzene with ethylene to produce ethylbenzene, and catalytic dehydrogenation of the ethylbenzene to produce styrene:

1. Catalytic alkylation of benzene with ethylene to ethylbenzene



2. Catalytic dehydrogenation of ethylbenzene to styrene



The first step in the process (Fig. III-1) is benzene drying to remove water from both feed and recycled benzene. The dry benzene (stream 1) is fed to the alkylation reactor along with ethylene, aluminum chloride catalyst, and recycled polyethylbenzenes. The reactor effluent goes to a settler, where crude ethylbenzene is decanted and the heavy catalyst-complex layer is recycled to the reactor. Reactor vent gas is routed though a condenser and scrubbers in the alkylation reaction section to recover aromatics and to remove HCl.

The crude ethylbenzene (stream 2) from the settler is washed with water and caustic to remove traces of chlorides and is then fed to the ethylbenzene purification section. The first step in purification is separation of recycled benzene (stream 3) from the crude ethylbenzene in the benzene recovery column. In the second step the product ethylbenzene (stream 4) is separated from the heavies in the ethylbenzene recovery column. Finally, the heavies are distilled in the polyethylbenzene column to separate the polyethylbenzenes, which are recycled (stream 5), from the residue oil.

Fresh ethylbenzene (stream 4) from the ethylbenzene purification section is combined with recycled ethylbenzene (stream 6) from the styrene purification section and fed to the heat exchanger in the dehydrogenation reaction section. Here the ethylbenzene is vaporized and superheated by heat exchange with the reactor effluent. Next, the superheated ethylbenzene vapor (stream 7) is mixed with superheated steam, and the combined stream is fed to the catalytic dehydrogenation reactor. The reactor effluent (stream 8) is cooled by heat exchange with the ethylbenzene feed. The mixture goes through a water-cooled condenser, where the steam and crude-styrene vapor are condensed and then flow to the separator. After separation, the noncondensible hydrogen-rich gas (stream 9) is sent to the recovery section, the process water condensate is decanted (stream 10) and goes to a stripper, and the remaining crude styrene (stream 11) is sent to the styrene purification section. The hydrogen-rich gas (stream 9) is compressed and then cooled in the recovery section to recover aromatic organics, which are returned to the process. After removal of the organics, the hydrogen-rich gas (stream 12) is usually sent to the steam superheater, where it is used as fuel. The process water condensate (stream 10) is fed to the process water stripper, where dissolved aromatic organics are removed and returned to the process. The purified water is sent to the plant boiler for use as boiler feed water.

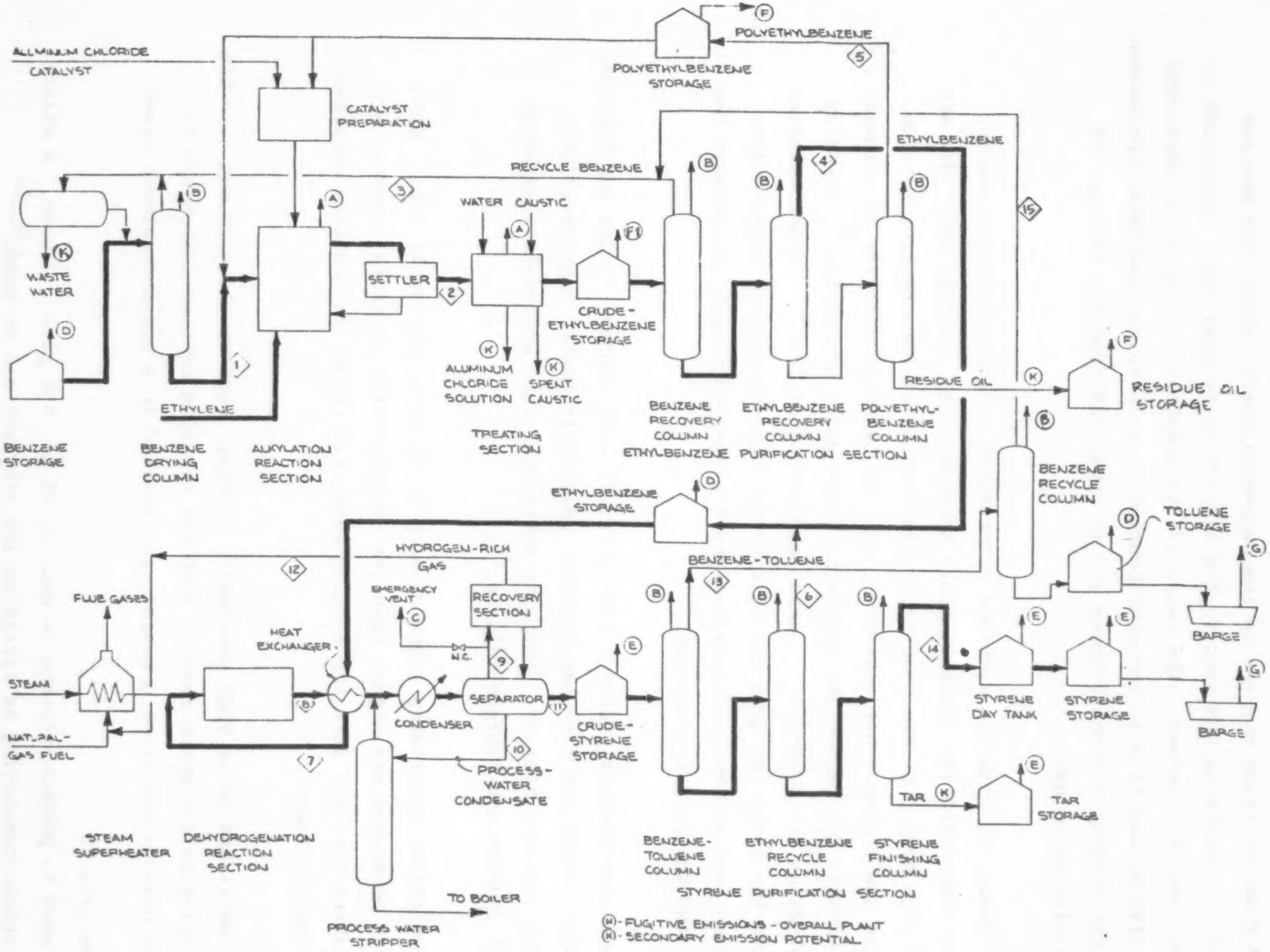

ALUMINUM CHLORIDE CATALYST
CATALYST PREPARATION
POLYETHYLBENZENE STORAGE
POLYETHYLBENZENE
F
5
ETHYLBENZENE
RECYCLE BENZENE
3
4
15
B
A
K
WASTE WATER
D
WATER
CAUSTIC
SETTLER
2
1
F1
CRUDE-ETHYLBENZENE STORAGE
ALUMINUM CHLORIDE SOLUTION
SPENT CAUSTIC
ETHYLENE
RESIDUE OIL
RESIDUE OIL STORAGE
BENZENE STORAGE
BENZENE DRYING COLUMN
ALKYLATION REACTION SECTION
TREATING SECTION
BENZENE RECOVERY COLUMN
ETHYLBENZENE RECOVERY COLUMN
POLYETHYLBENZENE COLUMN
ETHYLBENZENE PURIFICATION SECTION
ETHYLBENZENE STORAGE
BENZENE RECYCLE COLUMN
TOLUENE STORAGE
HYDROGEN-RICH GAS
BENZENE-TOLUENE
12
13
6
14
G
BARGE
FLUE GASES
EMERGENCY VENT
C
RECOVERY SECTION
N.C.
9
HEAT EXCHANGER
STEAM
8
SEPARATOR
11
E
CRUDE-STYRENE STORAGE
STYRENE DAY TANK
STYRENE STORAGE
NATURAL-GAS FUEL
7
CONDENSER
10
PROCESS-WATER CONDENSATE
TAR
TAR STORAGE
STEAM SUPERHEATER
DEHYDROGENATION REACTION SECTION
BENZENE-TOLUENE COLUMN
ETHYLBENZENE RECYCLE COLUMN
STYRENE FINISHING COLUMN
STYRENE PURIFICATION SECTION
TO BOILER
PROCESS WATER STRIPPER
(N)- FUGITIVE EMISSIONS - OVERALL PLANT
(N)- SECONDARY EMISSION POTENTIAL

Fig. III-1. Process Flow Diagram of Uncontrolled Model Plant for Production of Styrene from Benzene and Ethylene by Dehydrogenation of Ethylbenzene

In the styrene purification section, benzene and toluene (stream 13) are first separated from the crude styrene in the benzene-toluene column, and benzene (stream 15) is recovered and sent to the alkylation section after separation in the benzene recovery column. The recycled ethylbenzene (stream 6) is separated from the styrene and tars in the ethylbenzene recycle column and then reprocessed. Finally, the product styrene (stream 14) is separated from the tars in the styrene finishing column.

Any inert gases fed with the ethylene or produced in the alkylation reactor, along with some unreacted benzene, other organics, and hydrogen chloride, are exhausted from vent A of the reactor or from vent A of the treating section. The benzene and organics are recovered, and the hydrogen chloride is removed from the exhaust gas before the remaining inert gases are vented.[4] Normally these vent gases are routed to an emission-control device.[6,7] Other emission sources are the vents (B) from the columns for benzene drying, ethylbenzene purification, and styrene purification and the emergency vent (C) between the separator and the recovery section.[6,7]

Storage emission sources (vents D through F) include benzene, crude and finished ethylbenzene, crude and finished styrene, polyethylbenzene, benzene-toluene, residue oil, and tar storage. Handling emissions (vent G) result from barge loading of styrene and benzene-toluene.

Fugitive emissions occur when leaks develop in valves, pump seals, etc. When the process pressures are higher than the cooling-water pressure, benzene and other organics can leak into the cooling water and result in fugitive emissions from the cooling tower.

Secondary emissions occur when wastewater streams, such as the aluminum chloride catalyst solution and spent caustic from the treating section (discharge K), containing benzene and other organics, are treated in a waste-treatment plant.

2. Process Variations

Ethylene used to produce styrene is usually 95 to 99% pure. However, a dilute ethylene stream containing as little as 10% ethylene can be used.[8–11]

The pressure in the alkylation reactor can range from near-ambient to 2758 kPa, and temperatures may range from 80 to 400°C, depending on the pressure and the catalyst used. Aluminum chloride is the most common catalyst used in low-pressure liquid-phase processes. Some high-pressure vapor-phase processes using solid catalysts are in operation, such as the Alkar process by UOP and the newer Mobil/Badger process. The Mobil/Badger process was used in a demonstration unit at Foster Grant's Baton Rouge, LA, plant and in a converted ethylbenzene unit at Cosden Oil and Chemical's Big Spring, TX, plant. The Alkar process uses boron trifluoride as a catalyst for the alkylation of benzene with ethylene. El Paso Natural Gas Co. of Odessa, TX, uses a dilute ethylene stream (50%) to feed this process and sends the off-gases from the alkylation reactor to their boilers as fuel, thereby effectively reducing emission of volatile organic compounds (VOC) and recovering the fuel value of the non-ethylene hydrocarbons in the ethylene feed. It has been reported that this process does not produce by-products or sludge and that the catalyst lasts for several years.[9—11]

Another process variation is operation of the alkylation reactor at pressures greater than atmospheric with high-purity ethylene. Consequently natural gas has to be added at times to maintain the desired pressure in the reactor, and little, if any, emissions will vent from the reactor. The inert gases fed with the ethylene and natural gas and any inert gases produced as by-products in the reactor go with the alkylate to a degassing step, where they are removed when the pressure on the alkylate is reduced.[9]

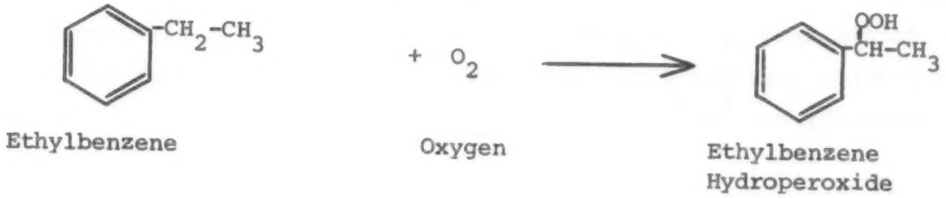
The dehydrogenation reactor can be operated either at constant temperature, which requires that heat be added in the reactor; or it can be operated under adiabatic conditions in which all the heat is supplied by diluting the ethylbenzene feed entering the reactor with superheated steam.[5,11]

The sequence of columns in the styrene purification section can be varied from that shown in Fig. III-1. The first separation takes a mixture of ethylbenzene, toluene, and benzene overhead, leaving the styrene and tars as bottoms. The overhead stream is then fed to a column where the benzene and toluene are separated from the ethylbenzene. The bottoms from the first separation go to another column, where the styrene is separated from the tars. In one process, only one condenser is used to condense the overhead vapor from three distillation columns: the benzene drying column, the benzene recovery column, and the column separating benzene from toluene.

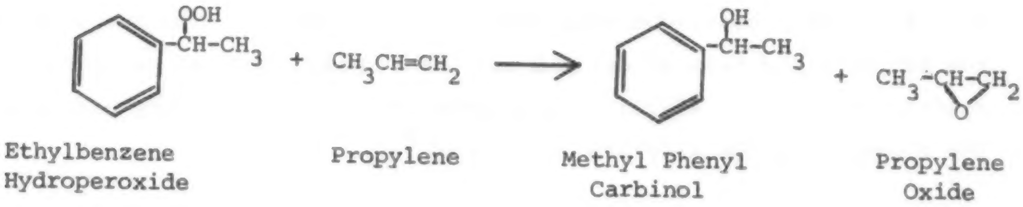
C. OTHER PROCESSES——STYRENE CO-PRODUCTION WITH PROPYLENE OXIDE

Ethylbenzene can be oxidized with air to make ethylbenzene hydroperoxide, which in turn is reacted with propylene to form methyl phenol carbinol and propylene oxide. The carbinol is dehydrated to styrene. The chemical reactions are shown below:

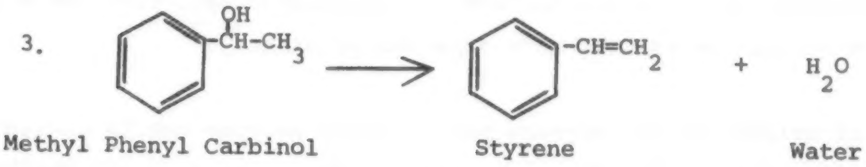
1.


-CH2-CH3
+ O2
OOH
-CH-CH3
Ethylbenzene
Oxygen
Ethylbenzene Hydroperoxide

2.


OOH
-CH-CH3
+ CH3CH=CH2
OH
-CH-CH3
+ CH3-CH-CH2
O
Ethylbenzene Hydroperoxide
Propylene
Methyl Phenyl Carbinol
Propylene Oxide

3.


OH
-CH-CH3
-CH=CH2
+ H2O
Methyl Phenyl Carbinol
Styrene
Water

About 2.5 kg of styrene is produced per kilogram of propylene oxide.[2,11,12]

Actual process data are currently not available. Since air is used for oxidation of ethylbenzene, the nitrogen from the air has to be vented; this is a possible source of VOC emissions.[13]

D. REFERENCES*

1. T. C. Gunn and K. L. Ring, "Benzene," pp 618.5022 V—Y in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (May 1977).
2. S. L. Soder, "Styrene," pp 694.3052 A, B in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (January 1977).
3. J. L. Blackford, "Propylene Oxide," p 690.8022 C in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (November 1976).
4. "Styrene," Hydrocarbon Processing, 56(11), 226—228 (1977).
5. J. W. Pervier et al., Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Houdry Division of Air Products, Inc., EPA-450/3-73-005-D (April 1974).
6. J. A. Key, IT Enviroscience, Inc., Trip Report for Visit to Dow Chemical, USA, Freeport, TX, July 28 and 29, 1977 (on file at EPA, ESED, Research Triangle Park, NC).
7. J. A. Key, IT Enviroscience, Inc., Trip Report for Visit to Cos-Mar Plant, Cosden Oil and Chemical Company, Carville, LA, July 16, 1977 (on file at EPA, ESED, Research Triangle Park, NC).
8. E. M. Carlson and M. G. Erskine, "Ethylene," pp 648.5054 H—I in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (February 1975).
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12. C. V. Sleeth, "Styrene Monomer," Chemical and Engineering Progress 73(11), 31—35 (1977).
13. L. R. Roberts, Texas Air Control Board Permit No. 2993, issued to Oxirane Chemical Co., Channelview, TX, for construction of propylene oxide—styrene monomer plant, Apr. 3, 1975.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Sections 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation. It should be noted that although ethane may be included in VOC emission totals in this report it does not, based on current research data, participate in ozone-forming reactions to an appreciable extent.

The process emissions estimated for the styrene model plant are based on the emissions reported in response[1] to EPA's requests for information from selected companies, the Cos-Mar[2] and Dow[3] trip reports, a Houdry study,[4] and SRI information and on engineering judgement. One source estimates that 30% of the 1976 capacity of the domestic styrene industry was from smaller, older, less efficient plants. These plants would be expected to have more emissions than newer, more efficient, and modern plants. Data received from styrene producers show wide variations in estimates of emissions, even from the more modern plants.

A. STYRENE FROM BENZENE-ETHYLENE

1. Model Plant

The model plant* for this study has a capacity of 300,000 Mg/yr, based on 8760 annual hours of operation.** Though not an actual operating plant, it is typical of many recently built plants. The model styrene process (Fig. III-1)

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*See p I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations the error introduced by assuming continuous operation is negligible.

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best fits today's styrene manufacturing and engineering technology. Single-process trains as shown are typical for the large plants built recently. The model process uses alkylation of benzene with ethylene in the presence of aluminum chloride catalyst to produce ethylbenzene. After purification, the ethylbenzene is dehydrogenated in the presence of steam over a solid catalyst to produce styrene. The crude styrene, separated from the hydrogen-rich gas and condensed steam, is purified to make the final product.

Typical raw material, intermediate, and product-storage tank capacities were estimated for a 300,000-Mg/yr plant. Storage-tank requirements are given in Sect. IV.A.2.d. Estimates of potential fugitive sources, based on data from existing facilities, are given in Sect. IV.A.2.e. Characteristics of the model plant that are important in air-dispersion modeling are shown in Appendix B.

2. Sources and Emissions

Emission rates and sources for the styrene process are summarized in Table IV-1.

a. Alkylation Reaction Vent——The alkylation reaction section vent gas (A, Fig. III-1) consists of unreacted ethylene and impurities such as methane and ethane. Some hydrogen chloride, unreacted benzene, and other aromatic organic vapors leave the reactor with the vent gas. The alkylation reaction section includes a condenser and a polyethylbenzene scrubber for recovering benzene and other aromatics from the vent gases. With high-purity ethylene (greater than 99.9%) the vent gases are almost nonexistent during normal operation. The amount of vent gases increases directly as the impurities (methane and ethane) in the ethylene increase. Data as to the purity of the ethylene were not available; so engineering judgement was used to estimate these emissions for the model plant. During the first few minutes of startup the quantity of vent gases temporarily increases, or until the alkylation reaction is fully established.

b. Column Vents——The gases from the benzene drying column and the columns in the ethylbenzene purification and styrene purification sections (vents B, Fig. III-1) are the noncondensibles that are dissolved in the feed to the columns, VOC that are not condensed, and, for the columns operated under vacuum, air that leaks into the column and is removed by the vacuum-jet systems. At one plant the gases from the process-water stripper condenser are vented to the atmosphere. The data available generally give the emissions for a group of distillation columns. Even when emissions from a single column are shown, the values are not consistent (see Appendix F), so that an estimate of the emissions from a single distillation step is questionable.[1] Engineering judgement was used to estimate the emissions shown in Table IV-1.

c. Emergency Vent on Separator——The hydrogen-rich gas from the separator also contains methane, ethane, ethylene, carbon dioxide, carbon monoxide, and aromatic organics, all of which are formed by side-reactions in the dehydrogenation reactor. It is vented only during an emergency shutdown of the recovery section. Normally aromatic organics are recovered and sent back to the process, and usually the hydrogen-rich gas is sent to the steam superheater, where it is burned as fuel. One plant vents it to the atmosphere and some plants send it to a flare.[1] Although benzene and VOC can be vented at significant rates during an emergency, the annual emission from the emergency vent is relatively insignificant, as is indicated in Table IV-1.

d. Storage and Handling Emissions——Emissions result from the storage and handling of benzene, ethylbenzene, styrene, and by-product and recycled streams. Sources for the model plant are shown in Fig. III-1 (sources D through G). Storage-tank conditions for the model plant are given in Table IV-2. The emissions in Table IV-1 were calculated based on fixed-roof tanks, half full, and a 8°C diurnal temperature, with use of the emission equations from AP-42.[6] However, calculated breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing-loss equation overpredicts emissions.[7]

Since benzene freezes at 5.5°C, storage tanks are heated to maintain the temperature above freezing if the ambient temperature drops below this point for a significant period. The styrene tar is heated to 115°C to reduce its viscosity. The styrene storage tanks are cooled to help inhibit polymerization. These temperature controls will reduce the emissions caused by breathing. No data were available on the amount of this reduction.

Emissions from loading of styrene and toluene barges were calculated with the equations from AP-42.[6] These emissions, included in Table IV-1, are 0.8 kg/hr.

Table IV-1. Estimates of Uncontrolled Benzene and Total VOC Emissions from Model Plant

Source	Vent Designation (Fig. III-1	Emissions Ratio (g/kg)[a] Benzene	Emissions Ratio (g/kg)[a] Total VOC	Emissions Rate (kg/hr) Benzene	Emissions Rate (kg/hr) Total VOC
Alkylation reaction[b] section	A	0.29	0.88	10	30
Column vents[c]	B	1.7	2.6	58	90
Emergency vent[d] on separator	C	0.003	0.008	0.091	0.27
Storage and handling	D-G	0.57	0.67	20	23
Fugitive	H	0.11	0.51	3.8	17
Secondary	K	0.067	0.088	2.3	3.0
Total		2.7	4.8	94	160

[a] g of emission per kg of product produced.

[b] See refs 1—3; estimated ethane content is 67%.

[c] See refs 3 and 4.

[d] Average rate for entire year, based on 80-kg/hr benzene and 240-kg/hr total VOC vented for 5 hr twice a year (from refs 3 and 4).

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Table IV-2. Model-Plant Storage Data

Content	Tank Size (m^3)	Turnovers per Year	Bulk Liquid Temperature (°C)
Benzene	10,000	40	25
Crude ehtylbenzene	300	6	30
Polyethylbenzene	80	6	50
Residue oil	160	60	65
Ethylbenzene	3,000	6	35
Crude styrene	900	6	50
Toluene	900	30	25
Styrene (3 tanks)	1,000	110	15
Styrene (2 tanks)	8,000	20	15
Styrene tar	160	60	115

Emissions from loading residue oil and tar into tank trucks are not significant because of their low vapor pressures.

e. Fugitive Emissions——Process pumps and valves are potential sources of fugitive emissions. The model plant is estimated to have 50 pumps handling VOC, with 10 in heavy liquid service and 40 in light liquid service (10 of these handle benzene). The estimated number of pipeline valves is 1000, with 160 in gas/vapor service (includes 32 handling benzene), 700 in light liquid service (includes 140 handling benzene), and 140 in heavy liquid service. The estimated number of safety/relief valves is 25 with 12 in gas/vapor service (includes 3 on benzene) 12 in light liquid service (includes 3 on benzene) and 1 in heavy liquid service. The fugitive emission factors from Appendix C were applied to this valve and pump count to determine the fugitive emissions shown in Table IV-1.

f. Secondary Emissions——Secondary VOC emissions can result from the handling and disposal of process-waste liquid streams. Five potential sources (K) are indicated in Fig. III-1 for the model plant.

For the model plant the total VOC-associated aqueous effluent is estimated to be 12,000 kg/hr and to contain 6 kg/hr VOC, of which 5 kg/hr is benzene. The aqueous effluent consists of the aluminum chloride solution and the spent caustic from the treating section, plus other miscellaneous wastewater streams such as the vacuum-system water discharges.[1,3] The secondary emission from the treatment of this aqueous waste is assumed to be 2.7 kg of VOC per hr, of which 2.3 kg is benzene. These values are included in the uncontrolled secondary emissions shown in Table IV-1.

The residue oil from the polyethylbenzene column and the tar from the styrene finishing column can be used as fuel or can be sold, depending on market conditions.[2,3] The total of the two streams is estimated to be 2000 kg/hr.[4] Based on the assumption that these streams are properly conditioned (by diluting with low-viscosity fuel oil or by heating) so as to reduce the viscosity and ensure proper atomization into an industrial boiler and that they otherwise meet the conditions specified in AP-42.[8] The resulting emissions are calculated to be 0.3 kg of VOC per hr. This value is included in the uncontrolled emissions, Table IV-1.

B. STYRENE CO-PRODUCTION WITH PROPYLENE OXIDE

No data are available on the actual process or emissions when styrene is co-produced with propylene oxide.

2C4

C. REFERENCES*

1. Responses to EPA request for information on emissions from ethylbenzene and styrene manufacturing; see Appendix E.

2. J. A. Key, IT Enviroscience, Inc., Trip Report on Visit to Cos-Mar Plant, Cosden Oil and Chemical Company, Carville, LA, June 16, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. J. A. Key, IT Enviroscience, Inc., Trip Report on Visit to Dow Chemical, USA, Freeport, TX, July 28 and 29, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

4. J. W. Pervier et al., Houdry Division of Air Products, Inc., Survey Reports on Atmospheric Emissions from the Petrochemical Industry, EPA-450/3-73-005-d (April 1974).

5. S. L. Soder and R. E. Davenport, "Ethylene," p 648.5054 N in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (January 1978).

6. C. C. Masser, "Storage of Petroleum Liquids," pp 4.3-12 and 4.3-13 in Compilation of Air Pollutant Emission Factors, AP-42, Part A, 3d ed. (August 1977).

7. E. C. Pulaski, TRW, letter dated May 30, 1979, to Richard Burr, EPA.

8. T. Lahre, "Fuel Oil Combustion," pp 1.3-1 to 1.3-5 in Compilation of Air Pollutant Emission Factors, AP-42, Part A, 3d ed. (August 1977).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. STYRENE FROM BENZENE-ETHYLENE

1. Alkylation Reaction Section

Some styrene producers control the vent gases from the alkylation reaction section by incinerating the process emissions from that section for use as a portion of the fuel for a fired heater or boiler. Since the vent stream would have already passed through a condenser and scrubbers for recovery of the aromatics and removal of HCl, no additional treatment would be needed before the vent stream is burned. When the ethylene feed stream to the alkylation reaction section is dilute, there is a strong economic incentive to use the methane, etc., as fuel.[1,2] To accomplish this a pipe is needed to transport the vent gas to the heater or boiler and a special burner and controls are required to prevent variations in the vent-gas flow and composition from disturbing the heater or boiler operation. For the model plant this stream is piped to the steam superheater.

Since the VOC burned is essentially equivalent to natural gas, the controlled VOC emissions in the steam superheater flue gas were calculated with the emission factors in AP-42,[3] and resulted in a VOC reduction efficiency of greater than 99.9% (see Table V-1).

2. Column Vents

The gases from the column vents are controlled by incineration in a flare and/or by a refrigerated vent condenser in many styrene plants. For the model plant the same flare is also used to control emissions from the styrene storage-tank vents as discussed in Sect. A.4.C. A flare-tip pressure drop of 3 in. of water was selected to provide low back pressure to the columns and storage tanks. A new plant can be designed so that a back pressure of this magnitude will not cause problems such as upsets in column operation or overpressure of the storage tanks. The flare system includes the manifold piping from the vents, provisions for a continuous purge-gas flow plus an oxygen-monitoring system to warn of possible explosive concentrations in the manifold piping, and a flare consisting of a knockout drum to remove liquid from the vent gases, a water seal, flare tip, pilot lights, steam ring, and all necessary controls,

Table V-1. Estimates of Controlled Benzene and Total VOC Emissions from Model Plant

Source	Stream Designation (Fig. III-1)	Control Device or Technique	Emission Reduction (%)	Emissions: Ratio (g/kg)[a] Benzene	Emissions: Ratio (g/kg)[a] Total VOC	Emissions: Rate (kg/hr) Benzene	Emissions: Rate (kg/hr) Total VOC
Alkylation reaction section	A	Process heater	99.9+	0.00004	0.0012	0.0014	0.0041
Column vents	B	Flare	99	0.017	0.026	0.58	0.90
Emergency vent on separator	C	Flare	99	0.000027[b]	0.000080[b]	0.00091[b]	0.0027[b]
Storage tanks	D	Internal-floating-roof tanks	85	0.085	0.090	2.9	3.1
Storage tanks	E	Pad vented to flare	99	0.000031	0.00050	0.0011	0.017
Storage tank	F1	Refrigerated vent condenser	80	0.00013	0.00025	0.0043	0.0087
Other storage and handling	F&G	None		0	0.015	0	0.53
Fugitive	H	Detection and correction of major leaks	74	0.029	0.14	0.98	4.7
Secondary	K	None		0.067	0.088	2.3	3.0
Total				0.20	0.36	6.8	12

[a] g of emission per kg of styrene produced.

[b] Average rate for entire year, based on emergency venting for 5 hr twice a year.

etc., to provide for automatic ignition and for steam application to ensure smokeless operation. An emission reduction of 99% was used to calculate the controlled benzene and VOC emissions given in Table V-1 for the column vents.[4]

3. Emergency Vent on Separator

The emergency vent on the separator releases hydrogen-rich gas that is controlled in many styrene plants by incineration in the same flare system used to control the gases from the column vents. For the model plant a separate flare is sized to handle only the emergency venting of gases from the separator when the compressor is shut down. A flare-tip pressure drop of 18 in. of water was used to size this flare. The decision to use one flare or multiple flares depends on the design philosophy of each company, and so a discussion of the factors involved is beyond the scope of this report. An emission reduction of 99% was also used to calculate the values given in Table V-1 for controlled benzene and VOC emissions from the separator emergency vent. This reduction is based on smokeless operation of the flare by use of assist steam. Because the gases to this flare contain over 90% hydrogen by volume, the capacity of the flare for smokeless operation with assist steam is believed to be approximately the same as the capacity calculated for a flare-tip pressure drop of 18 in. of water.[4]

4. Storage and Handling Sources

a. Benzene Storage——Control of benzene storage emissions will be discussed in a future EPA document. Information from styrene manufacturers indicates that benzene is stored in floating-roof tanks at seven locations and in fixed-roof tanks at the others.[5—9] A floating roof is commonly used to control storage-tank VOC emissions in the vapor-pressure range of benzene and is used in the model plant for storage emission control. The benzene emissions given in Table V-1 were calculated by assuming that a contact type of internal-floating roof* with secondary seals will reduce fixed-roof tank emissions by approximately 85%.[10]

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*Consist of internal floating covers or covered floating roofs as defined in API-2519, 2d ed, 1976 (fixed-roof tanks with internal floating device to reduce vapor loss).

b. Ethylbenzene and Toluene Storage—The vapor pressure of ethylbenzene under storage conditions in the model plant is 2.5 kPa and that of toluene is 4.0 kPa. The use of internal-floating-roof tanks for the model plant reduces the emissions from 1.0 to 0.15 kg of VOC per hour as calculated by assuming 85% control.[10] The emissions from these internal-floating-roof tanks are included in the emissions for floating-roof tanks given in Table V-1.

c. Styrene, Crude Styrene, and Tar Storage—Styrene, crude styrene, and tar stored in fixed-roof tanks will result in calculated average emissions of 1.7 kg VOC per hour. At two production plants the styrene storage tanks are blanketed with an inert gas to exclude air.[5,7] For the model plant these emissions are controlled by the same flare system used to control the vent gas from the columns as previously discussed. Using an emission reduction of 99%[4] gives a controlled emission of 0.017 kg/hr from the styrene, crude styrene, and tar storage tanks, as given in Table V-1.

d. Crude-Ethylbenzene Storage—The crude-ethylbenzene contains 40—60% benzene and is often warmer than ambient temperature. The temperature and level are relatively constant because normally the flows in and out are equal; therefore the breathing and working losses are small. A refrigerated vent condenser is used as the control on the model-plant crude-ethylbenzene storage vent. The emission reduction is estimated to be 80% and the calculated controlled emissions to be 0.0043 kg of benzene per hour and 0.0087 kg of VOC per hour.[11]

e. Other Storage and Handling—The storage of polyethylbenzene and residue oil in fixed-roof tanks results in a calculated average emission of less than 0.016 kg/hr, which is insignificant relative to other emissions from the process; therefore control is assumed not to be needed. The loading of barges with styrene and toluene results in an average emission of less than 0.51 kg VOC/hr as calculated with the AP-42 equations for submerged loading of barges.[12] The total uncontrolled emissions from these sources are 0.53 kg/hr of VOC (see Table V-1).

5. Fugitive Sources

Controls for fugitive sources are discussed in another EPA report.[13] Controlled fugitive emissions calculated from use of the factors given in Appendix C are included in Table V-1. The factors are based on the assumption that major leaks are detected and corrected and that the estimated emission reduction is 74%.

6. Secondary Sources

Secondary emissions caused by burning of the residue oil and tar streams as fuel are insignificant. The secondary emissions from the aqueous effluent from the treating section (streams K, Fig. III-1) are difficult to control. Control of secondary emissions is discussed in another EPA report.[14] No control system has been identified for the secondary emissions from the model plant.

B. OTHER PROCESSES——STYRENE CO-PRODUCTION WITH PROPYLENE OXIDE

Data are not currently available concerning control devices for the Oxirane process for styrene co-production with propylene oxide by the oxidation of ethylbenzene.

B. REFERENCES*

1. "Styrene," Hydrocarbon Processing 56(11), 226—228 (1977).

2. "Ethylbenzene," Hydrocarbon Processing 56(11), 151,152 (1977).

3. T. Lahre, "Fuel Oil Combustion," p 1.3-2, and "Natural Gas Combustion," p 1.4-2 in Compilation of Air Pollutant Emission Factors, AP-42, Part A, 3d ed. (August 1977).

4. V. Kalcevic, IT Enviroscience, Inc., Control Device Evaluation. Flares and the Use of Emissions as Fuels (in preparation for EPA, ESED, Research Triangle Park, NC).

5. Responses to EPA request for information on emissions from styrene and ethylbenzene manufacture, see Appendix E.

6. J. A. Key, IT Envirosicence, Inc., Trip Report on Visit to Cos-Mar Plant, Cosden Oil Chemical Company, Carville, LA June 16, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

7. J. A. Key, IT Enviroscience, Inc., Trip Report on Visit to Dow Chemical, USA, Freeport, TX, July 28-29, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

8. Responses to Texas Air Control Board 1975 Emission Inventory Questionnaire, see Appendix E.

9. Responses to Louisiana Air Control Commission 1975 Emission Inventory Questionnaire, see Appendix E.

10. William T. Moody, TRW, letter dated Aug. 15, 1979, to D. Beck, EPA.

11 D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (in preparation for EPA, ESED, Research Triangle Park, NC).

12. Supplement No. 7 for Compilation of Air Pollutant Emission Factors, AP-42, 2d ed., pp 4.5-5 to 4.4-6, EPA, OAQPS, Research Triangle Park, NC, April 1977.

13. D. G. Erikson, IT Enviroscience, Inc., Fugitive Emissions (in preparation for EPA, ESED, Research Triangle Park, NC).

14. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED, report, Research Triangle Park, NC).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. CONTROL COST IMPACT

The purpose of this section is to present estimated costs and cost-effectiveness data for control of benzene and total VOC emissions resulting from the production of styrene. Details of the model plant (Fig. III-1) are given in Sects. III and IV. Sample calculations are included in Appendix D.

The estimated capital costs represent the total investment, including all indirect costs such as engineering and contractors' fees and overheads that will be required for purchase and installation of all equipment and material to provide a facility as described. These are battery-limit costs and do not include the provisions for bringing utilities, services, or roads to the site, the backup facilities, the land, the research and development required, or the process piping and instrumentation interconnections that may be required within the process generating the waste gas. The costs are based on a new-plant installation; no retrofit cost considerations are included. Those costs are usually higher than the cost for a new-site installation for the same system and include, for example, demolition, crowded construction working conditions, scheduling construction activities with production activities, and longer interconnecting piping. These factors are so site-specific that no attempt has been made to provide costs. For specific retrofit cases rough costs can be obtained by using the new-site data and adding as required for a defined specific retrofit situation.

The annual costs include utilities, operating labor, maintenance supplies and labor, recovery credits, capital charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. The cost factors that were used are itemized in Table VI-1. Recovery credits are based on the market value of the raw materials for the material being recovered.

1. Styrene Process

a. Alkylation Reaction Section Vent——The estimated cost of a special burner system installed in the steam superheater to thermally oxidize benzene and total VOC emissions from the model-plant alkylation reaction section vent is $41,000 (see Table VI-2). This cost is based on the installation of piping, a

Table VI-1. Annual Cost Parameters

Operating factor	8760 hr/yr[a]
Operating labor	Negligible
Fixed costs	
Maintenance labor plus materials, 6%	29% of installed capital cost
Capital recovery, 18%[b]	
Taxes, insurances, administration charges, 5%	
Utilities	
Electric power	\$8.33/GJ (\$0.03/kWh)
Steam	\$5.50/Mg (\$2.50/thousand lb or million Btu)
Natural gas	\$1.90/GJ (\$2.00/thousand ft^3 or million Btu)
Heat recovery credits (equivalent to natural gas)	\$1.90/GJ (\$2.00/million Btu)

[a] Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations the error introduced by assuming continuous operation is negligible.

[b] Based on 10-year life and 12% interest.

Table VI-2. Emission Control Cost Estimates for Styrene Model Plant

			Annual Operating Costs			(B) Emission Reduction			(C) Cost Effectiveness (per Mg)[a]	
Emission Source	Control Device or Technique	Total Installed Capital Cost	Gross Annual	Recovery Credits	(A) Net Annual	Benzene (Mg/yr)	Total VOC (Mg/yr)	(%)	Benzene	Total VOC
Alkylation reaction section (A)[b]	Process heater	$41,000	$12,000	$38,000	($26,000)[c]	88	263	99.9+	(295)[c]	(99)[c]
Column vents and styrene storage tanks (B&E)	Flare	51,000	19,600	None	19,600	500	795	99	39	25
Emergency vent on separator (C)	Flare	60,000	18,700	None	18,700	0.79	2.4	99	24,000	7,900

[a] (C) = (A) ÷ (B).

[b] Vent designations shown on Fig. III-1.

[c] Savings.

compressor, a special burner, and all control instrumentation necessary to burn the low-pressure vent-gas stream in the steam superheater. Since the vent-gas rate varies directly with production, a plant twice the size of the model plant would have twice the emissions from this vent. Curve a of Fig. VI-1 was plotted to show the variation of installed capital cost of special burner systems with plant capacity.

To determine the cost effectiveness of the special burner system, an estimate was made of the gross annual cost (see Appendix D for sample calculations) and a recovery credit was calculated from the heating value of the vent gas. For the model plant the recovery credit is $38,000, resulting in a negative net annual cost (savings) of $26,000 (see curve A, Fig. VI-2). The variation of cost effectiveness with plant capacity is shown by curve A of Fig. VI-3 for control of benzene and by curve b for control of total VOC. Both show a negative cost effectiveness (or savings) at all plant capacities.

b. Column Vents——The vent streams (B, Fig. III-1) from the columns are controlled by connecting the vents to a flare system that is also used to control the emissions from the styrene storage-tank vents as discussed previously. The installed capital cost of this flare system was estimated to be $51,000 (see Table VI-2). The variation of the estimated installed capital cost of the flare system with plant capacity is shown by curve b of Fig. VI-1. The basis for these estimates is the installation of a complete flare system as described in the control device evaluation report on flares.[1] The estimated annual costs and the cost effectiveness for VOC and for benzene emission control are given in Table VI-2. Curve b of Fig. VI-2 is a plot of net annual cost of the flare system vs plant capacity, and curves c and d of Fig. VI-3 show the variation of cost effectiveness with plant capacity for benzene and for total VOC emission control.

c. Emergency Vent on Separator——Emissions from the emergency vent (C, Fig. III-1) on the separator are controlled by a second, larger, flare system. The installed capital cost of this flare system for the model plant was estimated to be $60,000 (see Table VI-2). The variation of the estimated installed capital cost of this flare system with plant capacity is shown by curve c of Fig. VI-1. These estimates are based on the installation of a complete flare system as

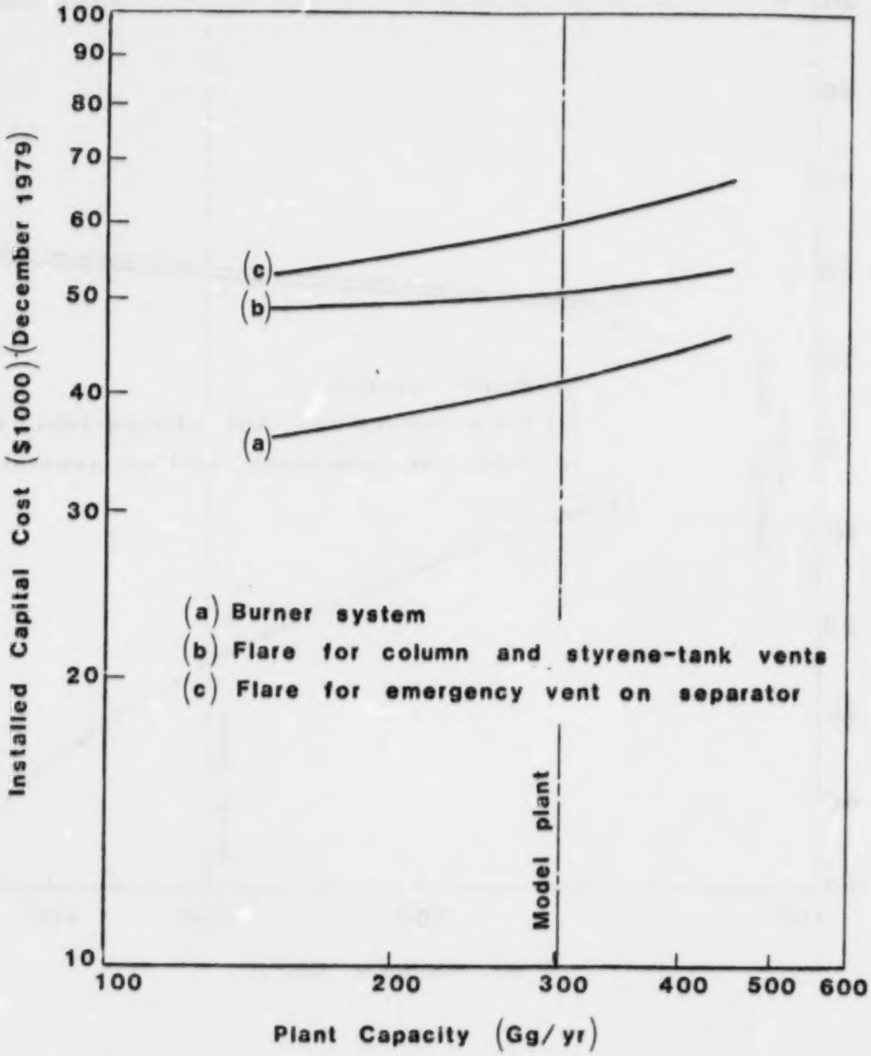

Fig. VI-1. Installed Capital Cost vs Plant Capacity for Emission Controls

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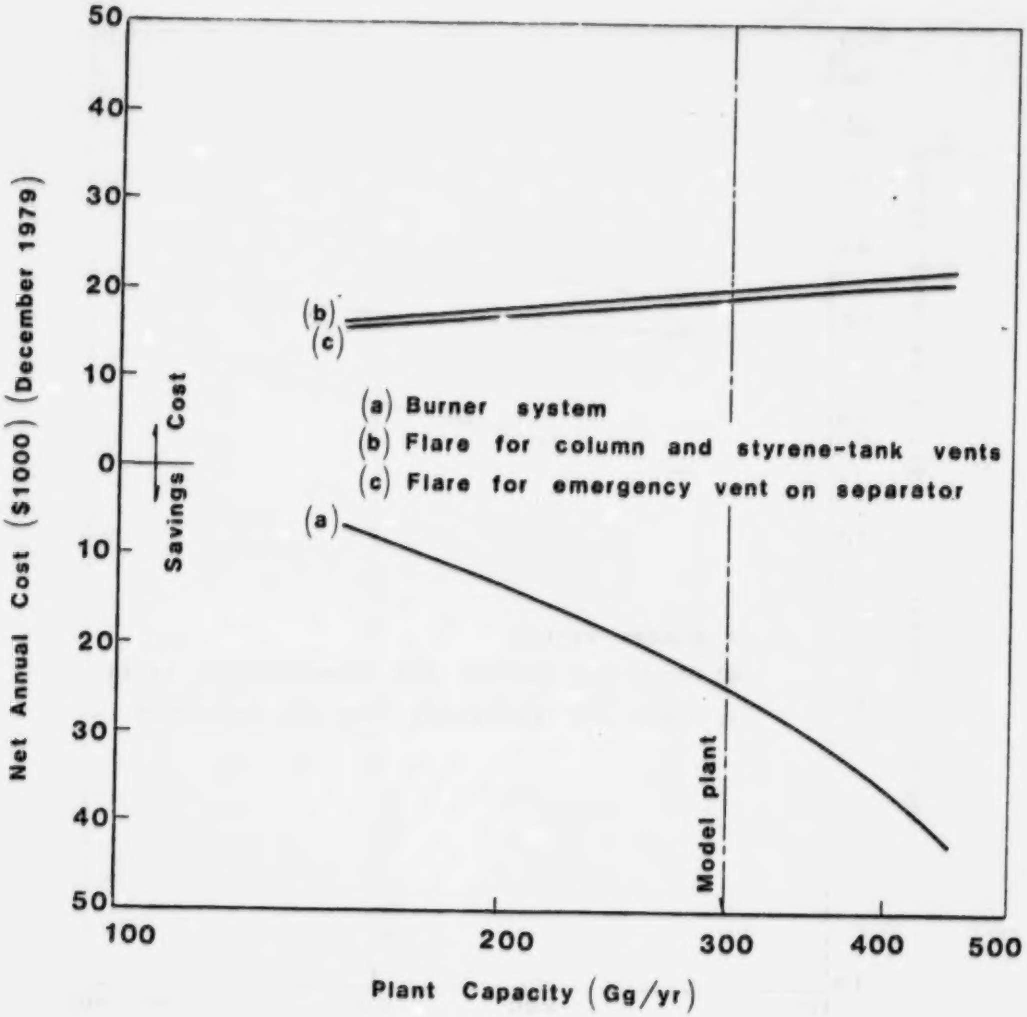

Fig. VI-2. Net Annual Cost or Savings vs Plant Capacity for Emission Controls

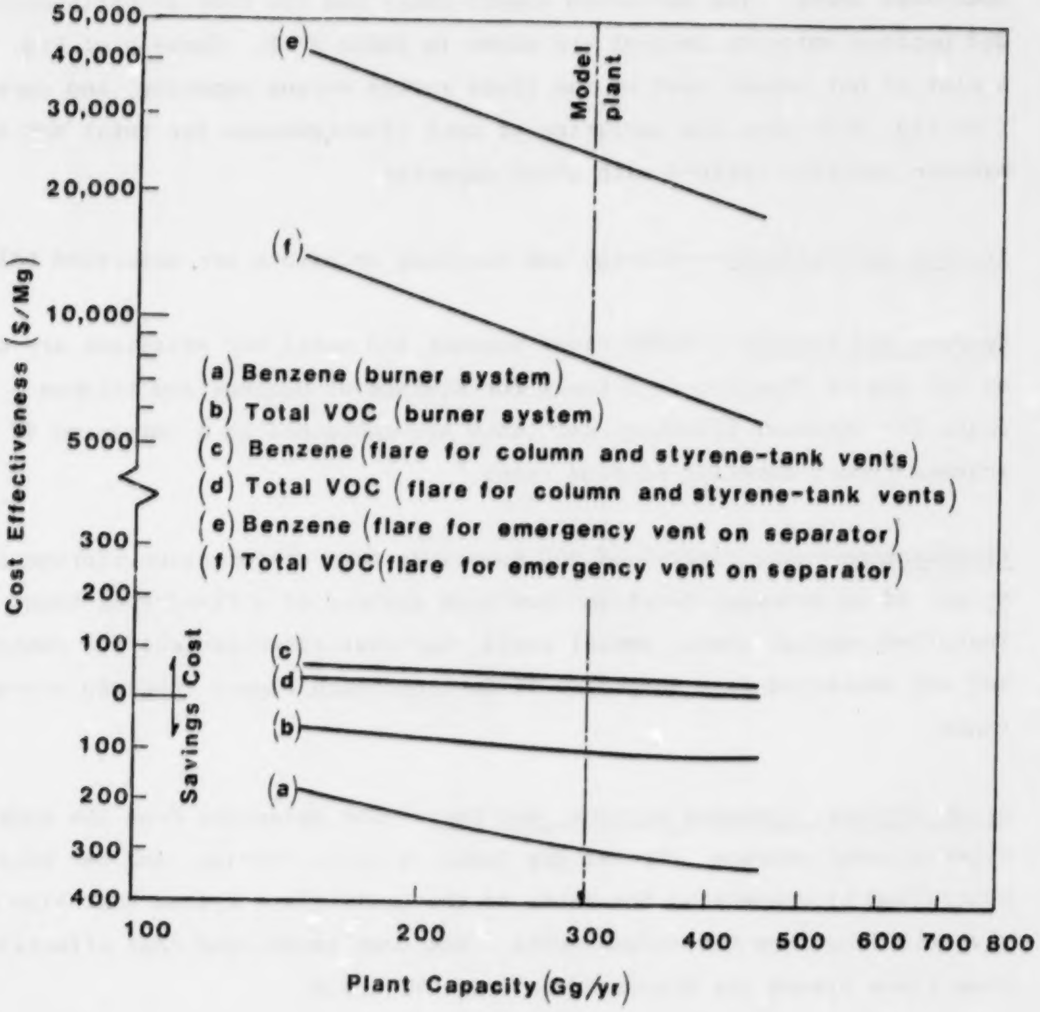

Fig. VI-3. Cost Effectiveness vs Plant Capacity for Emission Controls

described above. The estimated annual costs and the cost effectiveness for VOC and benzene emission control are given in Table VI-2. Curve c of Fig. VI-2 is a plot of net annual cost of the flare system versus capacity, and curves e and f of Fig. VI-3 show the variation of cost effectiveness for total VOC and for benzene emission control with plant capacity.

d. Storage and Handling——Storage and handling emissions are described below:

Benzene and toluene——Model-plant benzene and total VOC emissions are controlled by the use of floating-roof tanks for storage of benzene and toluene. The costs for internal floating-roof tanks are contained in a companion IT Enviroscience report covering storage tanks.[2]

Ethylbenzene——The control of VOC emissions from ethylbenzene storage is also by use of an internal-floating-roof tank instead of a fixed-roof tank. The installed capital costs, annual costs, and cost effectiveness for controlling VOC are contained in a companion IT Enviroscience report covering storage tanks.

Crude styrene, finished styrene, and tars——The emissions from the model-plant crude-styrene storage, styrene day tanks, styrene storage, and tar storage are controlled by connecting the vents to the small flare system that also controls the emissions from the column vents. The cost impact and cost effectiveness of this flare system are discussed in Sect. VI.A.1.b.

e. Fugitive Sources——A control system for fugitive sources is defined in Appendix C. A future document[3] will cover fugitive emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.

f. Secondary Sources——No control system has been identified for the secondary emissions from the model plant.

2. Other Processes——Styrene Coproduction with Propylene Oxide
No data are available to determine the cost of any control devices required to control emissions from the Oxirane process for styrene co-production with propylene oxide.

B. ENVIRONMENTAL AND ENERGY IMPACTS

1. Styrene Process

Table VI-3 shows the environmental impact of reducing benzene and VOC emissions by application of the described control systems to the model plant. From an energy standpoint a typical uncontrolled styrene process will require about 10,200 kJ/kg of styrene.[4] Individual impacts are discussed below.

a. Alkylation Reaction Section Vent—The special burner system installed in the steam superheater to control emissions from the alkylation reaction section vent reduces benzene emissions by 88 Mg/yr and total VOC emissions by 263 Mg/yr for the model plant. By utilizing the fuel value of the vent gas, 2300 MJ/hr of energy is recovered in the model plant. The energy effectiveness is (76) MJ/kg of VOC destroyed and (228) MJ/kg of benzene destroyed.

b. Column Vents, Emergency Vent on Separator, Crude-Styrene Storage, Styrene Day Tanks, Styrene Storage, and Tar Storage—The two flare systems reduce benzene emissions from these sources by 500 Mg/yr and total VOC emissions by 800 Mg/yr for the model plant. Generation of NO_x, CO, and smoke from flaring these emissions can have a negative impact on the environment if steam injection is not controlled carefully to ensure complete combustion.

Natural gas is required for the pilot lights and purge gas, and steam is used to ensure smokeless operation. The energy consumed is equivalent to 326 MJ/hr for the model plant, which is less than 0.1% of the total energy used by the model plant. The electrical energy required for the flare system and the oxygen monitor is negligible.

c. Other Emissions (Fugitive, Other Storage and Handling, and Secondary)—Control methods described for these sources are floating-roof storage tanks, refrigerated vent condenser, and repair of leaking components for fugitives. Application of these systems results in a VOC reduction of 260 Mg/yr for the model plant. The use of floating-roof storage tanks for emission control does not consume energy and has no adverse environmental or energy impacts.

Table VI-3. Environmental Impact of Controlled Model Plant

Emission Source	Stream or Vent Designation (Fig. III-1)	Control Device or Technique	Emission Reduction		
			(%)	Benzene (Mg/yr)	Total VOC (Mg/yr)
Alkylation reaction section	A	Process heater	99.9+	88	263
Column vents	B	Flare	99	500	780
Emergency vent on separator	C	Flare	99	0.79	2.4
Storage tanks	D	Internal-floating-roof tanks	85	140	150
Storage tanks	E	Pad vented to flare	99	0.92	15
Storage tank	F1	Refrigerated vent condenser	80	0.15	0.30
Other storage and handling	F&G	None			
Fugitive	H	Detection and correction of major leaks	74	24	110
Secondary	K	None			
Total				750	1300

2. Styrene Co-production with Propylene Oxide

Emission control systems for the Oxirane process for co-producing styrene with propylene oxide have not been described.

C. REFERENCES*

1. V. Kalcevic, IT Enviroscience, Inc., Control Device Evaluation. Flares and the Use of Emissions as Fuels (in preparation for EPA, ESED, Research Triangle Park, NC).

2. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (in preparation for EPA, ESED, Research Triangle Park, NC).

3. D. G. Erikson, IT Enviroscience, Inc., Fugitive Emissions (in preparation for EPA, ESED, Research Triangle Park, NC).

4. "Styrene," Hydrocarbon Processing," 56(11), 227 (1977).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VII. SUMMARY

Styrene is produced in the United States predominantly by the catalytic dehydrogenation of ethylbenzene. Ethylbenzene is manufactured by the catalytic alkylation of benzene with ethylene, usually in the same facility. In 1977 Oxirane started up a process that co-produces styrene and propylene oxide that accounts for about 11% of the current domestic styrene capacity of 3,986,000 Mg/yr.[1] Approximately 5% of the ethylbenzene capacity is located at petroleum refineries where ethylbenzene is distilled from mixed xylene streams.[2]

The styrene and ethylbenzene production annual growth rate is estimated to be 6% through 1982. The 1977 domestic styrene capacity is sufficient to meet the growth rate through 1982.[3] No shortage of either benzene or ethylene is expected during this period.[1]

Emission sources and control levels for the model plant are summarized in Table VII-1. The emissions projected for the domestic styrene industry in 1978 based on the estimated degree of control existing in 1978 are 2460 Mg/yr for benzene and 5670 Mg/yr for total VOC. These emission estimates are based on engineering judgement and data from individual styrene producers, state and local emission control agencies, and the open literature. The following individual projections were estimated:

	1978 Emissions (Mg/yr)	
Source	Benzene	VOC
Process	1000	2750
Storage and handling	1200	2300
Fugitive	60	340
Secondary	200	280
Totals	2460	5670

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[1] C. V. Sleeth, "Styrene Monomer," Chemical and Engineering Progress 73(11), 31—35 (1977).

[2] S. K. Paul and S. L. Soder, "Ethylbenzene - Salient Statistics," pp 645.3000 A—H in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (January 1977).

[3] S. L. Soder, "Styrene," pp 694.3052 A, B in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (January 1977).

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Table VII-1. Emission Summary for Model Plant

	Emission Rate (kg/hr)			
	Uncontrolled		Controlled	
Emission Source	Benzene	VOC	Benzene	VOC
Alkylation reaction vent	10	30	0.0014	0.0041
Column vents	58	90	0.58	0.90
Emergency vent on separator	0.091[a]	0.27[a]	0.00091[a]	0.0027[a]
Storage and handling	20	23	2.9	3.7
Fugitive	3.8	17	0.98	4.7
Secondary	2.3	3.0	2.3	3.0
Total	94	160	6.8	12

[a] Average rate for entire year, based on emergency venting for 5 hr twice a year.

The predominant emission points are the alkylation reaction vent, the column vents, and the storage-tank vents. The alkylation reaction vent gas can be controlled by piping it to the steam superheater for use as fuel, which would result in a removal efficiency of greater than 99% for both benzene and VOC. The cost of piping and a special burner for the model plant is estimated to be $41,000. The recovery credits are greater than the annual cost; therefore the net annual cost is negative; that is, a saving is realized. The column vents can be controlled by a flare with an estimated destruction efficiencey of 99%. The same flare can control the emissions from the styrene storage tanks, and its total installed cost is estimated at $51,000.

Benzene, ethylbenzene, and toluene storage emissions can be controlled by using covered floating-roof tanks. The emission reduction is estimated to be 85%.

APPENDIX A

Table A-1. Physical Properties of Ethylbenzene[a]

Property	Value
Synonyms	Ethylbenzol, phenylethane
Molecular formula	C_8H_{10}
Molecular weight	106.17
Physical state	Liquid
Vapor pressure	1284 Pa
Vapor specific gravity	3.66
Boiling point	136.2°C
Melting point	-94.97°C
Density	0.8670 g/ml at 20°C/4°C
Water solubility	0.014 g/100 ml of water[b]

[a] From: J. Dorigan, B. Fuller, and R. Duffy, "Ethylbenzene," p A II-246 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals D-E), MTR-7248, Rev 1, Appendix II, MITRE Corp., McLean, VA (September 1976).

[b] Handbook of Chemistry and Physics.

Table A-2. Physical Properties of Styrene[a]

Property	Value
Synonyms	Phenylethylene, vinylbenzene
Molecular formula	C_8H_8
Molecular weight	104.14
Physical state	Liquid
Vapor pressure	807 Pa
Vapor specific gravity	3.59
Boiling point	146°C
Melting point	-30.63°C
Density	0.9045 g/ml at 25°C/25°C
Water solubility	Insoluble

[a] From: J. Dorigan, B. Fuller, and R. Duffy, "Styrene," p AIV-156 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals O-Z), MTR-7248, Rev. 1, Appendix IV, MITRE Corp., McLean, VA (September 1976).

Table A-3. Physical Properties of Benzene[a]

Synonyms	Benzol, phenylhydride, coal naphtha
Molecular formula	C_6H_6
Molecular weight	78.11
Physical state	Liquid
Vapor pressure	95.9 mm at 25°C
Vapor density	2.77
Boiling point	80.1°C at 760 mm
Melting point	5.5°C
Density	0.8787 at 20°C/4°C
Water solubility	Slight (1.79 g/liter)

[a] J. Dorigan, B. Fuller, and R. Duffy, "Benzene," p AI-102 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals a-c)*, MTR-7248, Rev 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

APPENDIX B

Table B-1. Atmospheric Dispersion Parameters for 300,000-Mg/yr Model Plant

Source	Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temp. (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
Alkylation reaction section (uncontrolled)	2.8 (benzene) 8.3 (total VOC)	20	0.1	320	0.015	1.9
Steam superheater	0.001	60	3	550	35	4.5
Column vents (7) (uncontrolled)	2.3 ea (benzene) 3.6 ea (total VOC)	6	0.05 (7)	320	Neg.	Neg.
Emergency vent on separator (uncontrolled)	0 (normal)					
Storage and handling (Uncontrolled)						
Benzene	5.4	12.2	31.0	Ambient		
Crude ethylbenzene	0.012	6.1	7.9	305		
Polyethylbenzene	0.002	6.1	4.3	320		
Residue oil	0.003	6.1	5.5	340		
Ethylbenzene	0.12	12.2	18.3	310		
Crude styrene	0.06	9.1	11.0	320		
Toluene	0.16	9.1	11.0	Ambient		
Styrene (day) (3)	0.033 (ea)	9.1	11.6	290		
Styrene storage (2)	0.13 (ea)	12.2	29.0	290		
Tar	0.068	6.1	5.5	390		
Flare	0.16 (benzene)	12	0.1	1250		
Storage and handling (controlled)	0.26 (total VOC)					
Benzene	0.81	12.2	31.0	Ambient		
Crude ethylbenzene	0.002	6.1	7.9	305		
Polyethylbenzene	0.002	6.1	4.3	320		
Residue oil	0.003	6.1	5.5	340		
Ethylbenzene	0.018	12.2	18.3	310		
Crude styrene[a]						
Toluene	0.023	9.1	11.0	Ambient		
Styrene (day) (3)[a]						
Styrene storage (2)[a]						
Tar[a]						
Fugitive emissions[b] (uncontrolled)	1.04 (benzene) 4.8 (total VOC)					
Fugitive emissions[b] (controlled)	0.27 (benzene) 1.3 (total VOC)					
Secondary emissions (uncontrolled)	0.63 (benzene) 0.84 (total VOC)			Ambient		

[a] Controlled by flare.

[b] Fugitive emissions are evenly distributed over a rectangular area 50 m X 200 m.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

COST ESTIMATE AND ENERGY SAMPLE CALCULATIONS

This appendix contains an explanation and sample calculations for the estimated costs presented in this report.

The accuracy of an estimate is a function of the degree of data available when the estimate is made. Figure D-1 illustrates this relationship. The allowance indicated on this chart was included in the estimated costs to cover the undefined scope of the project.

The capital costs given in this report are based on a screening study, as indicated by Fig. D-1, which used general design criteria, block flowsheets, approximate material balances, and data on general equipment requirements. These costs have an accuracy range of +30% to -23% and provide an acceptable basis for determining the most cost-effective alternative.

A. USE OF ALKYLATION REACTOR VENT GASES AS FUEL-GAS SOURCE

This example is based on the estimated vent gases in the alkylation reaction section having an emission rate of 50 kg/hr (110 lb/hr) of total organics at 116°F. The VOC emission rate is 30 kg/hr based on the following composition:

Methane	40 wt%
Ethane	40 wt%
Benzene	20 wt%

The net heating value is 19,800 Btu/lb and the molecular weight is 24.5. The data for propylene in the control device evaluation report on flares and the use of emissions as fuel[1] can be used, but it is necessary to adjust the emission rate to a propylene equivalent because the molecular weight of propylene (42) is greater than that of the vent gas.

$$110 \text{ lb/hr} \times \frac{42}{24.5} = 190 \text{ lb/hr of propylene.}$$

1. Installed Capital Cost

Figure V-9 in the control device evaluation report on flares[1] shows that the installed capital cost a fuel-gas system for 190 lb/hr of propylene is $41,000.

2. Gross Annual Cost

Figure V-10 from the above-cited report[1] indicates that the gross annual operating cost for the above system is $12,000.

3. Credit

From Table VI-1 of this report the fuel credit is $2.00/million Btu. For the vent gas with a net heating value of 19,800 Btu/lb this is equal to a credit of $0.0396/lb of vent gas. For 100% of annual capacity operation the credit is

110 X 8760 X 0.0396 = $38,000/yr.

4. Annual Cost Summary

Gross	$12,000
Credit	(38,000)
Net	($26,000) savings

5. Cost Effectiveness

Cost effectiveness is the net annual operating cost ($26,000 savings) divided by the annual benzene or VOC destroyed at 99.9+% efficiency.

a. Annual VOC Destroyed——Based on a VOC emission rate of 30 kg/hr (0.003 Mg/hr)

0.03 X 8760 X 0.999 = 263 Mg/yr.

b. Cost Effectiveness (VOC)—— $\frac{(\$26,000)}{263}$ = ($99)/Mg of VOC destroyed.

c. Annual Benzene Destroyed——Based on a benzene emission rate of 10 kg/hr (0.01 Mg/hr)

0.01 X 8760 X 0.999 = 88 Mg/yr.

---

[1] V. Kalcevic, IT Enviroscience, Inc., Control Device Evaluation. Flares and the Use of Emissions as Fuels (in preparation for EPA, ESED, Research Triangle Park, NC).

d. Cost Effectiveness (Benzene)—— $\frac{(\$26{,}000)}{88}$ = ($295)/Mg of benzene destroyed.

6. **Energy Effectiveness**

Energy effectiveness is the net energy consumed (the energy consumed by the compressor minus the energy recovered by use of the vent gas as fuel) divided by the annual VOC destroyed at 99.9+% efficiency.

a. Electric Power Consumption——The electrical power consumption for compressing the vent gas must be calculated. For the model system the adiabatic horsepower required was calculated to be 2.4 (Eq. 6-23 on page 6-16 of Perry's Chemical Engineers Handbook, 5th ed., McGraw-Hill, was used). Based on the assumption of an 85% electric motor efficiency and an 85% compressor efficiency and converting horsepower to kilowatts (1 hp = 0.746 kW), the electric power consumption rate is

$$2.4 \times \frac{1}{0.85} \times \frac{1}{0.85} \times 0.746 = 2.48 \text{ kW.}$$

Annual energy used: convert kWh to joules ($1\text{MJ} = 2.778 \times 10^{-1}$ kWh):

$$\frac{2.48 \times 8760}{2.778 \times 10^{-1}} = 7.82 \times 10^{4} \text{ MJ/yr.}$$

Annual energy recovered: convert Btu to joules ($1 \text{ MJ} = 9.48 \times 10^{2}$ Btu):

$$\frac{110 \times 19{,}800 \times 8760}{9.48 \times 10^{2}} = 2.01 \times 10^{7} \text{ MJ/yr.}$$

Net annual energy:

$$7.83 \times 10^{4} - 2.01 \times 10^{7} = -2.005 \times 10^{7} \text{ MJ/yr (savings).}$$

b. Energy Effectiveness (VOC)—— $\frac{-2.005 \times 10^{7}}{263 \times 10^{3}}$ = -76 MJ/kg of VOC destroyed (savings).

c. Energy Effectiveness (Benzene)—— $\frac{(2.005 \times 10^{7})}{88 \times 10^{3}}$ = -228 MJ/kg of benzene destroyed (savings).

B. FLARE ON COLUMN VENT AND STYRENE STORAGE-TANK VENT EMISSIONS

This example is based on the estimated emissions from the column vents and styrene storage-tank vents. The maximum emission is estimated to be 1300 lb/hr at 105°F and to have a molecular weight of 31. The average emission is estimated to be 570 lb/hr containing 200 lb of VOC per hr of which 125 lb/hr is benzene.

1. Installed Capital Cost

The equation given in Appendix A of the flare report[1] was used to calculate the flare-tip diameter (2.95 in.) that would have a pressure drop of 3 in. H_2O when the vent gases are flared as described above at 1300 lb/hr. Figure B-1 in Appendix B of the same report shows that the installed capital cost of a total flare system of that size is $51,000.

2. Gross Annual Operating Cost

From Table VI-1 of this report the total fixed costs, including capital recovery, is 29% of the installed capital cost:

$$51{,}000 \times 0.29 = \$14{,}800/\text{yr}.$$

From Fig. IV-4 of the flare report[1] the natural gas used for the pilots is 60 scfh and for purging is 4 scfh. From Table VI-1 the cost of gas is $2.00 per thousand ft^3:

$$(60 + 4) \times 8760 \times \frac{2.00}{1000} = \$1100/\text{yr}.$$

From Sect. IV-A-1 of the flare report[1] it is estimated that 0.3 lb of steam is required per pound of emission; from Table VI-1 the cost of steam is $2.50/ thousand lb. The average emission is 570 lb/hr:

$$0.3 \times 570 \times 8760 \times \frac{2.50}{1000} = \$3700/\text{yr}.$$

The annual cost summary is as follows:

Fixed	$14,800
Natural gas	1,100
Steam	3,700
Total	$19,600

3. Cost Effectiveness

Cost effectiveness is the gross annual operating cost, $19,600, divided by the annual VOC or benzene destroyed at 99% efficiency. From Table VI-3 of this report the total VOC reduction for the column vents and the styrene storage-tank vents is 780 + 15 = 795 Mg/yr, and the total benzene destroyed is 500 + 0.92 = 500 Mg/yr:

$$\frac{\$19,600}{795} = \$25\text{/Mg of VOC destroyed.}$$

$$\frac{\$19,600}{500} = \$39\text{/Mg of benzene destroyed.}$$

APPENDIX E

LIST OF EPA INFORMATION SOURCES

H. M. Brennan, Amoco Chemicals Corp., letter to EPA, Mar. 6, 1978.

William G. Kelly, Atlantic Richfield Co., letter to EPA, Feb. 23, 1978.

L. T. Bufkin, American Hoechst Corp., letter to EPA, Jan. 26, 1978.

Charles R. Kuykendall, El Paso Products Co., letter to EPA, Jan. 31, 1978.

Frank E. Berry, Gulf Oil Chemicals Co., letter to EPA, Jan. 27, 1978.

Harry M. Keating, Monsanto Chemical Intermediates Co., letter to EPA, Apr. 28, 1978.

F. D. Bess, Union Carbide Corp., letter to EPA, May 5, 1977.

Theodore M. Nairn, Jr., Cosden Oil & Chemical Co., Texas Air Control Board 1975 Emissions Inventory Questionnaire.

Ray Warren, El Paso Products Co., Texas Air Control Board 1975 Emissions Inventory Questionnaire.

Alvin J. Pokorny, Foster Grant Co., Louisiana Air Control Commission Emissions Inventory Questionnaire (Oct. 13, 1975).

Harry M. Walker, Monsanto Co., Chocolate Bayou plant, Texas Air Control Board 1975 Emissions Inventory Questionnaire.

L. R. Roberts, Texas Air Control Board Permit No. 2993, issued to Oxirane Chemical Company (Channelview) for construction of a propylene oxide-styrene monomer plant, Apr. 3, 1975.

J. L. Laird, Sun Oil Co. of Pennsylvania, Texas Air Control Board 1975 Emissions Inventory Questionnaire.

Val D. Dutcher, Union Carbide Corp., Texas Air Control Board 1975 Emissions Inventory Questionnaire.

R. C. Parnell, Amoco Chemicals Corp., EPA Questionnaire.

E. R. Hendrick, Monsanto Co., Texas City plant, EPA Questionnaire (Oct. 6, 1972).

Frank Berry, Dow Chemical Co., EPA Questionnaire (Aug. 25, 1972).

W. E. Holmes, Dow Chemical USA, Texas Division, EPA Questionnaire (Aug. 17, 1972).

James M. Black, Cos-Mar Co., EPA Questionnaire (Sept. 8, 1972).

Milton K. Dawson, Sinclair-Koppers Company, Kobuta plant, EPA Questionnaire (Sept. 8, 1972).

J. D. Martin, Union Carbide Corp., EPA Questionnaire (Aug. 23, 1972).

APPENDIX F

EXISTING PLANT CONSIDERATIONS

Table F-1 lists process control devices reported in use by industry. Tables F-2 through F-4 give data on reported uncontrolled emissions from several producers that show the variability in composition and flow.

As is described in Sect. III of this report, several variations of the processes for production of ethylbenzene and styrene are possible. Some of these variations influence the amount and rate of emissions. Such variations and the resulting influence on emissions should be considered before it is decided to retrofit control devices into existing plants.

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

Table F-1. Control Devices Currently Used by the Domestic Styrene Industry[a]

Company	Emission Source			
	Alkylation Reaction Section	Column Vents	Emergency Vent on Separator	Storage Tank Vents
American Hoechst Corp.	Flare or absorber	Vent condensers[b]	NR[c]	Vent condenser[b]
Amoco Chemicals Corp.	Flare[b]	Flare[b]	Flare	NR
Atlantic Richfield Co.	Absorber[b]	Vent condensers[b]	NR	Floating-roof tanks and conservation vents[b]
Cos-Mar, Inc.	Flare[b]	Flare[b]	Flare	Floating-roof tanks and conservation vents[b]
Dow Chemical, USA	Process heater	Flare and process heater	Absorber	Floating-roof tanks, flares, and conservation vents[b]
El Paso Natural Gas Co.	Boilers[d]	Flare and vent condenser	NR[e]	Conservation vents[b]
Gulf Oil Corp.	Flare[b]	Flare[b]	Flare	Floating-roof tanks and conservation vents[b]
Monsanto Co.	Absorbers[b]	Vent condensers[b]	Flare	Floating-roof tanks[b]
Union Carbide Corp.	Process heater	Process heater and vent condensers	NR	Vent condenser and floating-roof tanks[b]

[a] See Appendix A.

[b] Some vents go directly to the atmosphere.

[c] Not reported.

[d] Dilute ehtylene feed stock to reactor and off-gases used as fuel.

[e] Gases vent to atmosphere after going through recovery section.

[f] During startup some vents go through a scrubber to the atmosphere.

Table F-2. Reported Uncontrolled Emission from Various Alkylation Reactor Vents[a]

Company	Component	Composition (wt %)	Emission Ratio[b] (g/kg)
Dow	Hydrocarbons	45—50	1.1—1.5
	Hydrogen chloride	45—55	1.1—1.6
Monsanto (reactor vent)	C_1 and C_2 hydrocarbons	20	0.08
	Inert gases	80	0.31
	HCl and aromatics	Trace	
Monsanto (wash system vent)	C_1 and C_2 hydrocarbons	20.78	0.078
	Aromatics (includes benzene)	6.88	0.026
	(Benzene)	(5.19)	0.020
	Inert gases	72.42	0.27
Arco[c]	Methane and ethane	58	6.0
	Benzene	13	1.3
	Carbon dioxide	29	3.0
Gulf[c]	Methane and ethane	81	0.23
	Benzene	19	0.06
	Hydrogen chloride	Some	

[a] See Appendix E.

[b] g of emission per kg of ethylbenzene produced.

[c] Based on design data; not measured.

Table F-3. Reported Uncontrolled Emissions from Various Column Vents[a]

Company	Component	Composition (wt %)	Emission Ratio (g/kg)[b]
Monsanto Co.	Organics (includes benzene)	46	5.1
	(Benzene)	(44)	(4.9)
	C_1, C_2, C_3, C_4, C_5 hydrocarbons	27	3.0
	Inert gases	27	3.0
El Paso Natural Gas	Benzene	1.7	0.6
	Toluene	0.8	0.3
	Ethylbenzene	0.8	0.3
	Styrene	0.8	0.3
	Water	96.1	34.5
Sun Oil	Benzene	36	0.29
	Other organics	21	0.16
	Water	8	0.07
	Inert gases	35	0.28
Amoco[c]	Benzene	27	0.4
	Other organics	9	0.1
	Inert gases	64	1.0
Arco[d]	Aromatics	58	7.8
	Other organics	0.88	0.1
	Inert gases	41	5.5

[a] See Appendix E.

[b] g of emission per kg of styrene produced.

[c] Based on design data; not measured.

[d] Based on design calculations for 3 vacuum-column vents only; no data on atmospheric column vent or on vents from columns in ethylbenzene purification section.

Table F-4. Reported Uncontrolled Emissions from
Two Vents on Two Vacuum-Column Jets
at Sun Oil Co.[a]

	Composition (wt %)			
		From EB and BT Columns[b]		
Component	From Styrene Column As of 4-21-76, 3:00 pm	As of 4-20-76, 4:00 pm	As of 4-21-76, 2:00 pm	1974 Average
Benzene	29	46	47	19
Other organics	11	23	22	19
Water	10	12	10	4
Inert gases	50	19	21	58

[a] See Appendix E.

[b] The discharges from the vacuum jets on the ethylbenzene (EB) column and on the benzene-toluene (BT) column are piped together for one emission (BT) source.

REPORT 6

CAPROLACTAM

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ENVIRONMENTAL PROTECTION AGENCY
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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch² (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1×10^{12} grams
G	giga	10^{9}	1 Gg = 1×10^{9} grams
M	mega	10^{6}	1 Mg = 1×10^{6} grams
k	kilo	10^{3}	1 km = 1×10^{3} meters
m	milli	10^{-3}	1 mV = 1×10^{-3} volt
μ	micro	10^{-6}	1 μg = 1×10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTING CAPROLACTAM

Caprolactam production was selected for study because the total estimated emissions of volatile organic compounds (VOC) from its manufacture were projected to be high and include some benzene, which is used as a solvent in the process.

Caprolactam is a solid at normal room conditions; however, the material may be stored or transferred in molten form. Physical property data are given in Appendix A.

B. CAPROLACTAM USAGE AND GROWTH

Table II-1 gives a breakdown of caprolactam uses. Almost all the caprolactam manufactured in the United States is used in the production of nylon fibers, resins, and films. In 1976, 354 Gg of caprolactam was produced domestically. The total domestic consumption was 337 Gg; exports amounted to 13.2 Gg; and imports were negligible. Of the 337 Gg consumed, 311 Gg was used to produce nylon fibers, and 25 Gg went into production of nylon resins and films. The remainder was consumed in a variety of miscellaneous applications, such as the formulation of specialty coatings, textile stiffeners, adhesives, floor-polish additives, and brush bristles.[1]

Through 1981 caprolactam consumption is expected to increase at the rate of 5 to 6% per year. Caprolactam consumption for nylon fiber, which is greatly influenced by the use of nylon for rugs and carpets, is expected to increase at 5 to 6% per year. Consumption of caprolactam for nylon resins is expected to increase at 7 to 9% per year because of the increased demand for nylon resins in the automotive and electronics industries.[1]

Caprolactam availability and cost depend on the availability and cost of the raw materials phenol and benzene. The price of caprolactam during 1977 was at 52 to 54¢/lb. Price increases are expected in the future due to higher raw-material costs, increased capital costs, and higher energy costs.[1]

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Table II-1. Domestic Caprolactam Consumption[a]

End Use	1976 Caprolactam Consumption (Gg)	Percent of Total Consumption
Nylon-6 fibers	310.7	92.2
Nylon-6 resins and films	25.0	7.4
Miscellaneous	1.4	0.4
Total	337.1	100.0

[a] See ref 1.

C. DOMESTIC PRODUCERS

Currently three plants are being operated by three producers manufacturing caprolactam in the United States.[1] Table II-2 lists the producers, locations, capacities, process used, and raw-material source. Figure II-1 shows the plant locations.

Caprolactam is manufactured from cyclohexanone in a three-step process. Two variations on the conventional process are practiced, the BASF process and the DSM/HPO (Stamicarbon) process, which differ mainly in the production of the key intermediate and in the amount of by-product ammonium sulfate produced. All three plants have captive production for the cyclohexanone feed, which is manufactured, together with cyclohexanol, as a co-product by either cyclohexane oxidation or phenol reduction.[2—5]

Allied Chemical has the largest capacity and consumes most of its caprolactam in the production of nylon-6 fibers and resins. Nipro sells all the caprolactam that it produces. Badische consumes about one-third of its caprolactam captively and markets the remainder.[1]

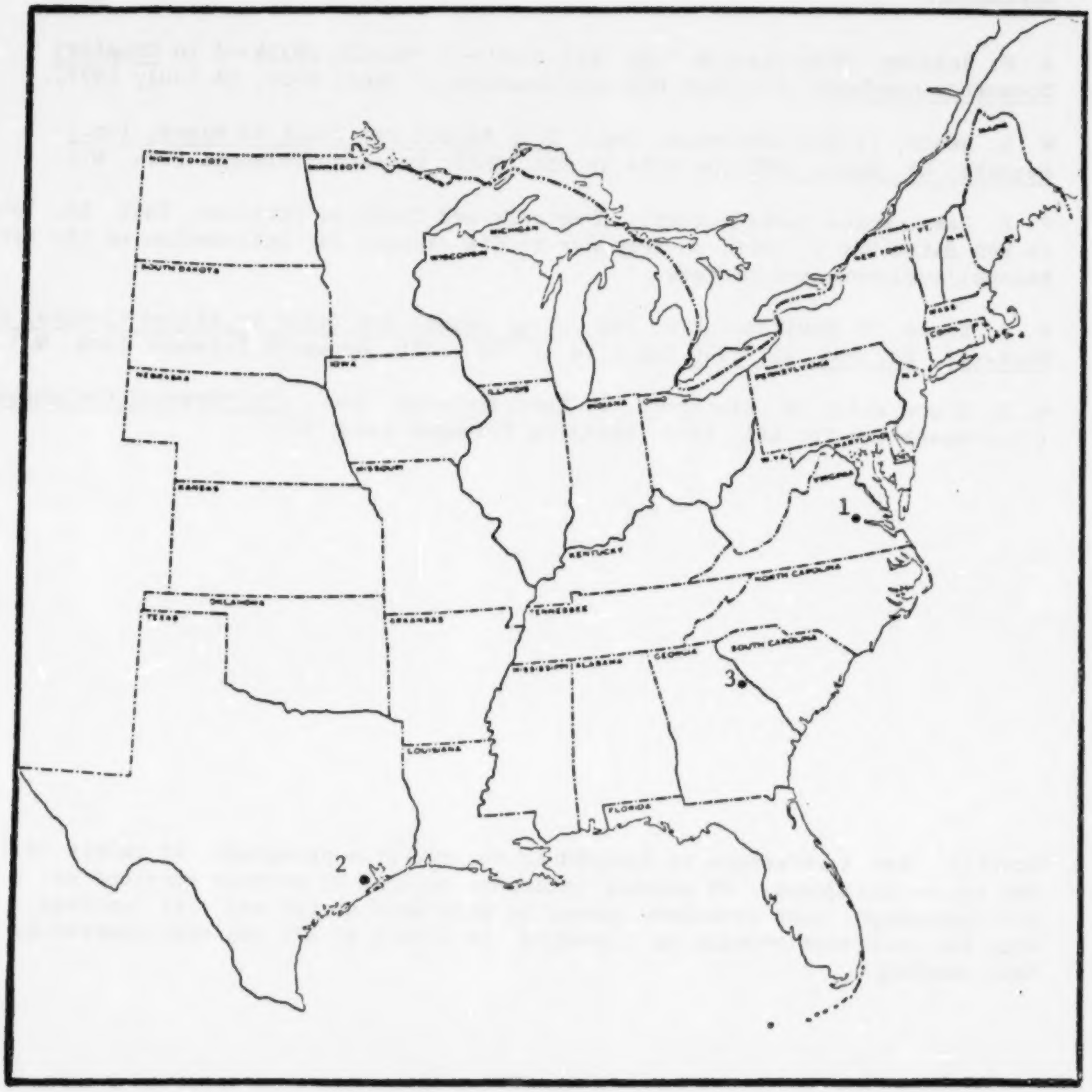
Table II-2. Caprolactam Producers

Company	Location	Annual Production Capacity (Gg) (May 1977)	Process Used	Caprolactam Raw Material Source
Allied Chemical Fibers Division	Hopewell, VA	191[a]	Conventional	Phenol
Badische Co.	Freeport, TX	159[a]	BASF	Cyclohexane
Nipro, Inc.	Augusta, GA	140[b]	DSM/HPO[c] (Stamicarbon)	Cyclohexane
Total		490		

[a] See ref 1.

[b] See ref 2.

[c] Nipro also uses the conventional process for part of caprolactum production.


NORTH DAKOTA
MINNESOTA
SOUTH DAKOTA
WISCONSIN
MICHIGAN
NEW YORK
NEBRASKA
IOWA
ILLINOIS
INDIANA
OHIO
PENNSYLVANIA
KANSAS
MISSOURI
KENTUCKY
1
NORTH CAROLINA
TENNESSEE
OKLAHOMA
TEXAS
ARKANSAS
SOUTH CAROLINA
3
MISSISSIPPI
ALABAMA
GEORGIA
LOUISIANA
FLORIDA
2

1. Allied Chemical Corp., Hopewell, VA
2. Badische Co., Freeport, TX
3. Nipro, Inc., Augusta, GA

Fig. II-1. Locations of Plants Manufacturing Caprolactam

D. REFERENCES*

1. R. F. Bradley, "Caprolactam," pp. 625.2031C—D and 625.2032A—T in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (July 1977).

2. W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Nipro, Inc., Augusta, GA, April 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. F. D. Bess, Union Carbide Corp., Chemicals and Plastics Division, Taft, LA, letter to EPA dated May 5, 1978, in response to EPA request for information on the cyclohexanol/cyclohexanone process.

4. W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Allied Chemical Co., Hopewell, VA, Feb. 21, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

5. W. D. Bruce and J. W. Blackburn, IT Enviroscience, Inc., Cyclohexanol/Cyclohexanone (in preparation for EPA, ESED, Research Triangle Park, NC).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

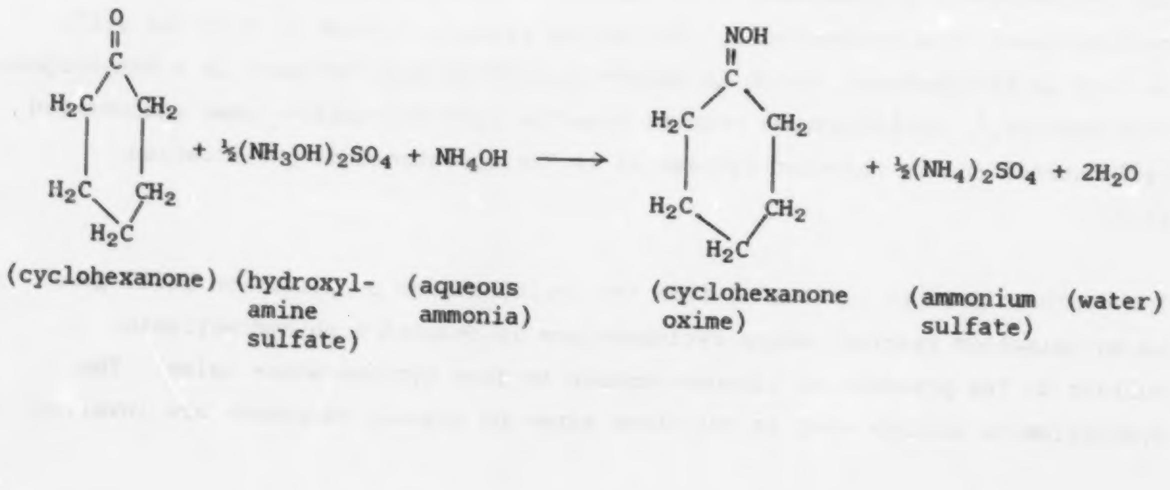
The three domestic processes for producing caprolactam utilize the same synthesis route in that they start with cyclohexanone, but they differ in the use or preparation of key hydroxylamine salt intermediates. The conventional process uses hydroxylamine sulfate prepared by the Rashig process as the key intermediate. This process is used by Allied Chemical for all its production and by Nipro for about 20% of its production. The BASF process, which is used by Badische, also uses hydroxylamine sulfate, but it is prepared by an alternative route that produces less ammonium sulfate by-product. In the DSM/HPO (Stamicarbon) process, used by Nipro for about 80% of its production, hydroxylamine phosphate is the key intermediate.[1]

B. CAPROLACTAM PRODUCTION PROCESSES

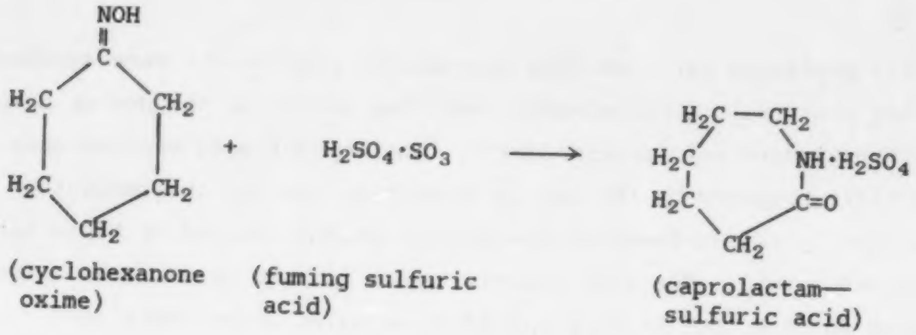
1. Conventional Process

In the conventional method ammonium nitrile, which is obtained by oxidation of ammonia and absorption in ammonia carbonate solution, and ammonia are used to absorb sulfur dioxide to produce hydroxylamine disulfonate. Subsequent hydrolysis yields hydroxylamine sulfate and ammonium sulfate.[1] Hydroxylamine sulfate is then reacted with cyclohexanone to produce caprolactam, as shown by the following reactions:

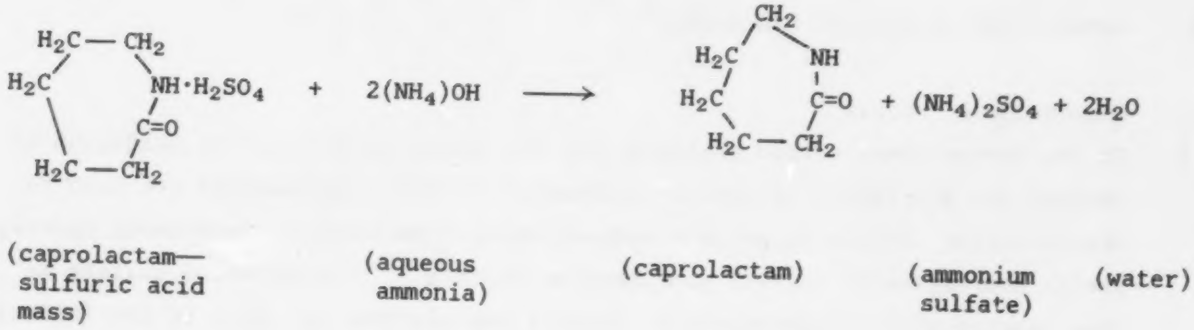
Reaction 1: Conventional Cyclohexanone Oximation


O
C
H_2C
CH_2
H_2C
CH_2
H_2C
+ ½$(NH_3OH)_2SO_4$ + NH_4OH
NOH
C
H_2C
CH_2
H_2C
CH_2
H_2C
+ ½$(NH_4)_2SO_4$ + $2H_2O$
(cyclohexanone)
(hydroxylamine sulfate)
(aqueous ammonia)
(cyclohexanone oxime)
(ammonium sulfate)
(water)

Reaction 2: Beckmann Rearrangement


NOH
C
H2C
CH2
+
$H_2SO_4 \cdot SO_3$
NH·H2SO4
C=O
(cyclohexanone oxime)
(fuming sulfuric acid)
(caprolactam—sulfuric acid)

Reaction 3: Neutralization


NH·H2SO4
C=O
+
$2(NH_4)OH$
NH
+ $(NH_4)_2SO_4$ + $2H_2O$
(caprolactam—sulfuric acid mass)
(aqueous ammonia)
(caprolactam)
(ammonium sulfate)
(water)

The flow diagram for the manufacture of caprolactam by the conventional process is shown by Fig. III-1.[2—4] The indicated process vents are discussed in Sect. IV. The cyclohexanol/cyclohexanone feed (stream 1) enters a still for separation of cyclohexanone from cyclohexanol. The bottom product (stream 2) from the still is rich in cyclohexanol, which is dehydrogenated to cyclohexanone in a dehydrogenation reactor.[5] Cyclohexanone product from the reactor contains some unconverted cyclohexanol and is recycled (stream 3) to the cyclohexanone purification still.

The overhead product (stream 4) from the cyclohexanone purification still goes to an oximation reactor, where cyclohexanone is reacted with hydroxylamine sulfate in the presence of aqueous ammonia to form cyclohexanone oxime. The hydroxylamine sulfate step is not shown since no organic compounds are involved.

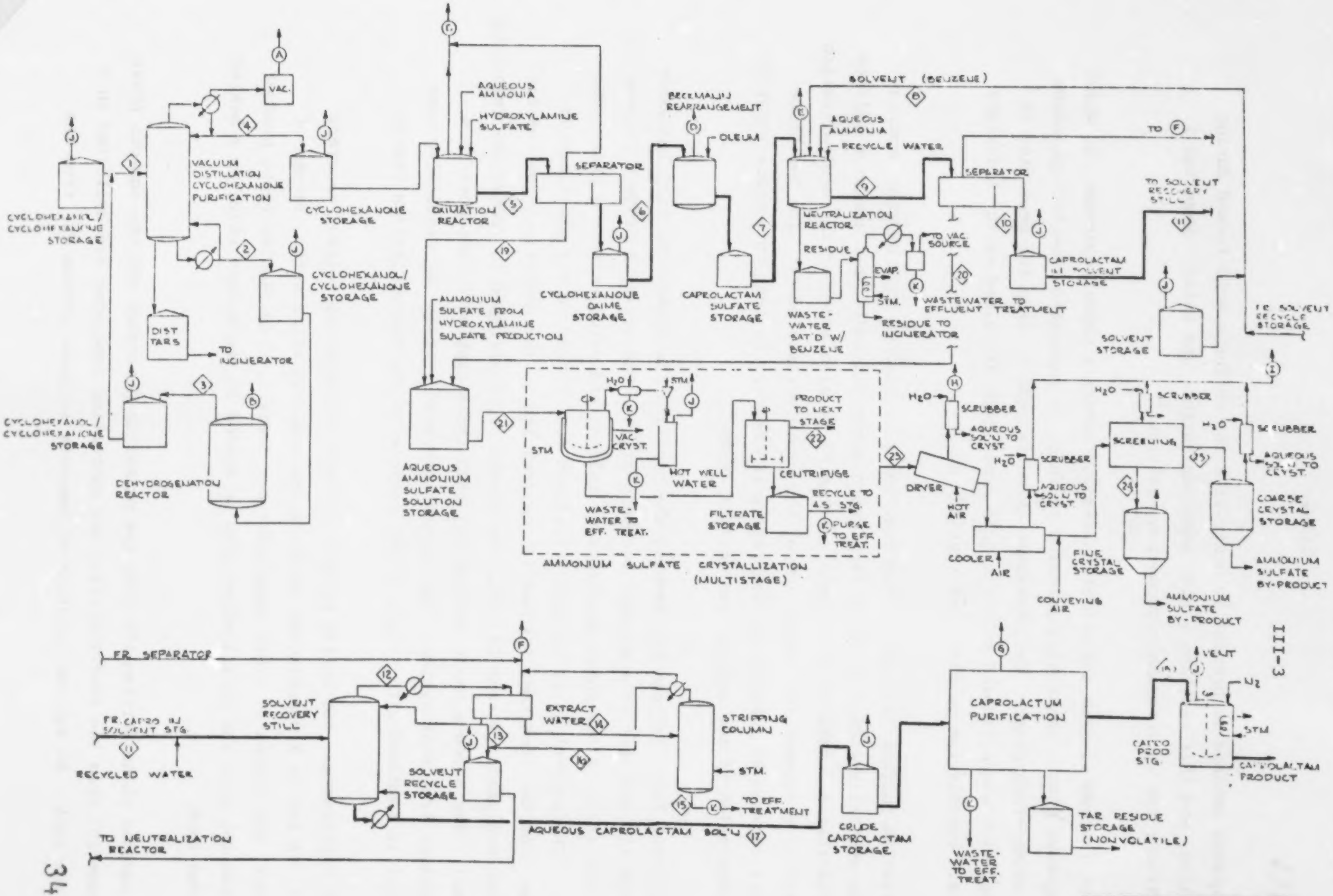

CYCLOHEXANOL / CYCLOHEXANONE STORAGE
VACUUM DISTILLATION CYCLOHEXANONE PURIFICATION
VAC.
CYCLOHEXANONE STORAGE
CYCLOHEXANOL / CYCLOHEXANONE STORAGE
DIST TARS
TO INCINERATOR
CYCLOHEXANOL / CYCLOHEXANONE STORAGE
DEHYDROGENATION REACTOR
AQUEOUS AMMONIA
HYDROXYLAMINE SULFATE
OXIMATION REACTOR
SEPARATOR
AMMONIUM SULFATE FROM HYDROXYLAMINE SULFATE PRODUCTION
CYCLOHEXANONE OXIME STORAGE
BECKMANN REARRANGEMENT
OLEUM
CAPROLACTAM SULFATE STORAGE
SOLVENT (BENZENE)
AQUEOUS AMMONIA
RECYCLE WATER
NEUTRALIZATION REACTOR
RESIDUE
WASTE-WATER SAT'D W/ BENZENE
EVAP.
STM.
TO VAC. SOURCE
WASTEWATER TO EFFLUENT TREATMENT
RESIDUE TO INCINERATOR
SEPARATOR
TO F
TO SOLVENT RECOVERY STILL
CAPROLACTAM IN SOLVENT STORAGE
SOLVENT STORAGE
FR. SOLVENT RECYCLE STORAGE
AQUEOUS AMMONIUM SULFATE SOLUTION STORAGE
STM
H_2O
STM
VAC. CRYST.
HOT WELL WATER
WASTE-WATER TO EFF. TREAT.
PRODUCT TO NEXT STAGE
CENTRIFUGE
FILTRATE STORAGE
RECYCLE TO A.S. STG.
PURGE TO EFF. TREAT.
AMMONIUM SULFATE CRYSTALLIZATION (MULTISTAGE)
H_2O
SCRUBBER
AQUEOUS SOL'N TO CRYST
DRYER
HOT AIR
COOLER
AIR
CONVEYING AIR
H_2O
SCRUBBER
AQUEOUS SOL'N TO CRYST.
H_2O
SCRUBBER
SCREENING
FINE CRYSTAL STORAGE
AMMONIUM SULFATE BY-PRODUCT
H_2O
SCRUBBER
AQUEOUS SOL'N TO CRYST.
COARSE CRYSTAL STORAGE
AMMONIUM SULFATE BY-PRODUCT
FR. SEPARATOR
FR. CAPRO IN SOLVENT STG.
RECYCLED WATER
SOLVENT RECOVERY STILL
SOLVENT RECYCLE STORAGE
EXTRACT WATER
STRIPPING COLUMN
STM.
TO EFF. TREATMENT
AQUEOUS CAPROLACTAM SOL'N
TO NEUTRALIZATION REACTOR
CRUDE CAPROLACTAM STORAGE
CAPROLACTUM PURIFICATION
WASTE-WATER TO EFF. TREAT
TAR RESIDUE STORAGE (NONVOLATILE)
VENT
N_2
STM
CAPRO PROD STG.
CAPROLACTAM PRODUCT
A
B
C
D
E
F
G
H
I
J
K
1
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Fig. III-1. Process Flow Diagram for Manufacture of Caprolactam - Conventional Process

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The aqueous ammonia is present to neutralize the sulfuric acid formed during omxiation, and this reaction yields ammonium sulfate and water. Reaction 1 illustrates the cyclohexanone oximation reaction.[1]

Product (stream 5) from the oximation reactor enters a phase separator, in which the aqueous phase, containing ammonium sulfate, is separated from the cyclohexanone oxime—rich phase. Cyclohexanone oxime (stream 6) from the separator is reacted with oleum (fuming sulfuric acid containing dissolved sulfur trioxide) to yield caprolactam sulfate; see reaction 2.

Caprolactam sulfate (stream 7) from reaction 2 is reacted with aqueous ammonia in the neutralization reactor to form caprolactam and additional ammonium sulfate; see reaction 3. Benzene or toluene (stream 8) is also added to the neutralization reactor as a solvent for extraction of the caprolactam product. The two-phase mixture (stream 9) leaving the neutralization reactor is sent to a phase separator for separation of the aqueous and solvent layers.

The solvent layer (stream 10) leaving the separator is mixed with recycled water (stream 11) and sent to a solvent recovery still. The overhead product (stream 12) from the still, a two-phase azeotrope of solvent and water, enters a phase separator. The solvent layer is partly utilized for recycle to the distillation column, and the remainder (stream 13) is recycled to the neutralization reactor. The aqueous phase (stream 14) from the separator is stripped to remove the remaining solvent. The aqueous phase (stream 15) from the stripping column goes to a wastewater treatment system. The solvent overhead (stream 16) containing some product is combined with stream 13 for recycle to the neutralization reactor.

Crude caprolactam, the bottom product (stream 17) from the solvent recovery still, is fed to a caprolactam purification step, in which water, traces of solvent, and traces of other impurities are removed. Caprolactam final product (stream 18) from the purification step is stored in the molten state in a heated storage tank.

The aqueous phase (stream 19) from the oximation separator and the aqueous phase (stream 20) from the neutralization and extraction separator are collected in a storage tank. An aqueous solution of ammonium sulfate (stream 21) from the tank is processed in the ammonium sulfate recovery system. Stream 21 goes to vacuum crystallization and then to a centrifuge for removal of the mother liquor. The crystalline ammonium sulfate product (stream 22) from the centrifuge is fed to the next crystallization stage. Ammonium sulfate (stream 23) from the last crystallization stage is dried, cooled, and then screened to separate the fine and coarse product crystals. Final ammonium sulfate product (streams 24 and 25) is collected in storage bins. Scrubbers for particulate control are shown on all three lines leading to vent I.

The details of caprolactam purification are not covered here because these steps are considered to be confidential by the producers interviewed for this study.

2. Process Variations

a. BASF Process——This process, which is used by Badische, varies from the conventional process in the method by which hydroxylamine sulfate is prepared. Nitric oxide is prepared by oxidation of ammonia with oxygen in the presence of steam and is then reduced with hydrogen over a platinum catalyst on carbon suspended in a dilute sulfuric acid solution to yield hydroxylamine sulfate.[1] The production of ammonium sulfate is practically eliminated in this step. In the rest of the process the conventional process route is followed. The amount of ammonium sulfate generated while in contact with VOC is the same for both processes; therefore the process variation is not expected to significantly affect organic emissions.[6]

b. DSM/HPO (Stamicarbon) Process——In this process variation, which is used by Nipro, the hydroxylamine phosphate solution is prepared by hydrogenation of nitrate ions with the aid of a noble-metal catalyst in a buffered phosphate solution. Hydroxylamine phosphate solution is reacted with a stream containing cyclohexanone in the presence of toluene, which extracts the product, cyclohexanone oxime. The cyclohexanone oxime is then separated from the toluene by distillation. The DSM/HPO method completely eliminates the production of ammonium sulfate in phosphate preparation and in cyclohexanone oximation. The remainder of the process is conventional. Benzene emissions are eliminated by the use of toluene as solvent. No significant additional organic emissions result from this deviation from the conventional process, as indicated by the emissions data supplied by Nipro.[2]

Nipro also indicates a variation in their technique for purification of caprolactam. Crude caprolactam product is purified by ion exchange, followed by hydrogenation. No VOC process emissions are indicated by Nipro for this segment of their caprolactam process.[2]

C. REFERENCES*

1. R. F. Bradley, "Caprolactam," pp 625.2031C—D and 625.3032A—T in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (July 1977).
2. W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Nipro, Inc., Augusta, GA, Apr. 18, 1978 (on file at EPA, ESED, Research Triangle Park, NC).
3. Significant Organic Products, p 121, EPA-440/1-75/045.
4. M. Taverna and M. Chiti, "Compare Routes to Caprolactam," Hydrocarbon Processing, pp 134—137 (November 1970).
5. McKetta and Cunningham, "Adipic Acid," pp 129—146 in Encyclopedia of Chemical Processing and Design, vol 2, Dekker Publishing Co., New York, 1971.
6. Dow Badische Company, emissions data in Emissions Inventory Questionnaire, submitted to Texas Air Control Board, Mar. 19, 1976.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. MODEL PLANT FOR CAPROLACTAM PRODUCTION

The model plant for caprolactam manufacture has a capacity of 70 Gg/yr, based on 8760* hr of operation per year. Although not an actual operating plant, it has a capacity corresponding to that of the average-size process train now being employed in caprolactam manufacture. The model plant shown by Fig. III-1 represents current technology for manufacture of caprolactam by the conventional process.

B. SOURCES AND EMISSIONS

1. General

Uncontrolled emission rates and sources for the model plant are summarized in Table IV-1. The emission rates were obtained by averaging information from the three producers.[1—4] Storage and handling and fugitive emissions from SOCMI will be covered by separate EPA documents.[5,6] Potential storage emission sources are indicated on Fig. III-1 by the letter J and for secondary emissions by the letter K.

2. Process Emissions

The major emissions of benzene and total VOC occur from the cyclohexanone purification vent (A, Fig. III-1) and from the phase-separation, solvent recovery, and stripping vents (F, Fig. III-1). Benzene occurs as an impurity in the feed

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*Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations the error introduced by assuming continuous operation is negligible.

Table IV-1. Uncontrolled Emissions from Model-Plant Caprolactam Manufacture by Conventional Process

		Emissions			
	Stream Designation (Fig.III-1)	Ratio (g/kg)[a]		Rate (kg/hr)	
Emission Source		Benzene	Total VOC	Benzene	Total VOC
Cyclohexanone purification	A	0.16	3.1	1.27	24.8
Dehydrogenation reactor[b]	B		NA[b]		NA
Oximation reactor and separator	C		0.024		0.19
Rearrangement	D		0.00011		0.0009
Neutralization reactor	E	0.0043	0.04	0.034	0.32
Phase separation, solvent recovery, and stripping	F	0.21	2.0	1.68	16.0
Caprolactum purification	G		0.13		1.04
Ammonium sulfate drying[c]	H		0.6		4.8
Ammonium sulfate cooling, screening, storage, and loading[c]	I		0.055		0.44
Total		0.37	5.95	2.98	47.59

[a] g of emission per kg of caprolactam produced.

[b] Data not available.

[c] Water scrubbers needed for ammonium sulfate recovery are part of the process and are not considered to be a control device.

to the cyclohexanone purification distillation column. The total VOC emission can vary, depending on the vacuum system design and operation. Benzene is used as a solvent to extract the caprolactam product, and subsequent recovery is the source of the emission from vents F.

Hydrogen produced in the cyclohexanol dehydrogenation reaction is emitted from vent B and the stream can contain significant VOC. Data on the composition and flow are not available. Normally this stream is burned as fuel.

The second largest process VOC emission source is the ammonium sulfate crystallization dryer vent (H). Figure III-1 indicates the use of water scrubbers on all lines to vents H and I. These scrubbers are for particulate removal and ammonium sulfate reovery and are considered to be part of the process.

The other VOC process emissions occur from the oximation reaction and separator vent (C), rearrangement vent (D), neutralization reactor vent (E), caprolactam purification vent (G), and ammonium sulfate cooling, screening, storage, and loading vent (I).

5. Secondary Emissions

Secondary VOC emissions can result from the handling and disposal of such process waste liquid streams as the residue from the neutralization reactor and the streams from the solvent stripping column and the caprolactam purification and ammonium sulfate crystallization steps. The model-plant wastewater flow rate is estimated to be 550 Mg/hr, with a total carbon composition of 480 ppm. The components of the wastewater include caprolactam, cyclohexanone oxime, cyclohexanol, and cyclohexanone.[1,3] Evaluation of the potential secondary emissions from the SOCMI is covered by a secondary emissions report.[7]

C. PROCESS VARIATIONS

The VOC emissions from the process and DSM/HPO (Stamicarbon) processes are very similar to the conventional process emissions except that with the DSM/HPO process benzene is replaced by toluene as the solvent.

C. REFERENCES*

1. W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Allied Chemical Company, Hopewell, VA, Feb. 21, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

2. F. L. Piguet, Allied Chemical, Hopewell, VA, letter dated Sept. 28, 1979, to D. R. Patrick (EPA).

3. W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Nipro, Inc., Augusta, GA, Apr. 18, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

4. Badische Company, emissions data on cyclohexanol/cyclohexanone and caprolactam production facilities supplied in response to EPA-114 letter request, May 12, 1978.

5. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (in preparation for EPA, ESED, Research Triangle Park, NC).

6. D. G. Erikson, IT Enviroscience, Inc., Fugitive Emissions (in preparation for EPA, ESED, Research Triangle Park, NC).

7. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

Control devices currently being used to control VOC emissions from the manufacture of caprolactam are shown in Appendix B. The projected effect of using these control devices to reduce the uncontrolled emissions from the conventional process model plant (Table IV-1) is shown by Table V-1. The costs and cost effectiveness for these applications have not been determined.

A. CONVENTIONAL PROCESS

1. Cyclohexanone Purification Vent

One of the large sources of of benzene and total VOC emissions is the cyclohexanone purification vent (A, Fig. III-1). A 90% reduction of emissions by use of a vent gas condenser is reported by one producer.[1] A 90% reduction efficiency was also used to project the emission reduction for the model plant (Table V-1).

2. Dehydrogenation Reactor Vent

The emission from this vent (B) is primarily composed of hydrogen formed from the conversion of cyclohexanol to cyclohexanone and is normally used as fuel. Although data on the VOC content are not available, the destruction efficiency is expected to exceed 99%. This is in agreement with the emission destruction efficiency listed in AP-42 for natural gas burned in an industrial process boiler.[2]

3. Neutralization and Solvent Processing Vents

The emissions from vents E and F contain benzene plus other VOC and are normally controlled by vent stream condensers. For the controlled emissions listed in Table V-1 an efficiency of 70% was used for the emissions from vent E and 90% for the emissions from vent F. These efficiencies were reported by one producer.[1]

4. Ammonium Sulfate Drying and Handling Vents

The emissions from vents H and I are from the water scrubbers needed to control and recover ammonium sulfate. These water scrubbers are not considered to be emission control devices even though they do achieve a VOC reduction of about 50%. A control device is not normally used to control the emissions from these vents and is not included for the model plant.

Table V-1. Controlled Emissions from Model-Plant Caprolactam Manufacture by Conventional Process

Emission Source	Stream Designation (Fig.III-1)	Control Device or Technique	Emission Reduction (%)	Emissions Ratio (g/kg)[a] Benzene	Emissions Ratio (g/kg)[a] VOC	Emissions Rate (kg/hr) Benzene	Emissions Rate (kg/hr) VOC
Cyclohexanone purification	A	Condenser	90	0.016	0.31	0.13	2.5
Dehydrogenation reactor[b]	B	Used as fuel	>99				
Oximation reactor and separator	C	None			0.024		0.19
Rearrangement	D	None			0.00011		0.0009
Neutralization reactor	E	Condenser	70	0.0013	0.012	0.01	0.096
Phase separation, solvent recovery, and stripping	F	Condenser	90	0.021	0.20	0.17	1.6
Caprolactum purification	G	None			0.13		1.04
Ammonium sulfate drying[c]	H	None			0.6		4.8
Ammonium sulfate cooling, screening, storage, and loading[c]	I	None			0.055		0.44
Total				0.038	1.33	0.31	10.67

[a] g of emission per kg of caprolactam produced.

[b] No emission data available.

[c] Water scrubbers needed for ammonium sulfate recovery are part of the process and are not considered to be a control device.

5. Other Process Vents

Emissions from the other process vents (C, D, and G) are normally not controlled and are left uncontrolled for the model plant. These emissions do not contain benzene.

B. PROCESS VARIATIONS

There is only one significant emission change resulting from caprolactam manufacture by another process. Benzene emissions from the neutralization reaction and solvent processing steps are eliminated with the DSM/HPO (Stamicarbon) process because toluene is used as the solvent instead of benzene.

C. REFERENCES*

1. Badische Company, emission data in Emissions Inventory Questionnaire, submitted to Texas Air Control Board, Mar. 19, 1976.

2. T. Lahre, "Natural Gas Combustion," pp. 1.4-1—1.4-3 in Compilation of Air Pollutant Emission Factors, 3d ed., Part A, AP-42 (August 1977).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. TYPICAL PLANT

The environmental impact of the application of the described control system to the model plant would be a VOC emission reduction of 323 Mg/yr and a benzene emission reduction of 23 Mg/yr.

B. INDUSTRY[1—3]

The caprolactam industry appears to be using the level of control indicated for the controlled model plant. The domestic production of caprolactam in 1979 is projected to be 415 Gg. On this basis total industry emissions are projected to be 16 Mg of benzene and 554 Mg of total VOC during 1979. This does not include the fugitive, secondary, or storage and handling emissions that are expected to be typical of SOCMI.

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C. REFERENCES*

1. Badische Company, emission data in Emissions Inventory Questionnaire, submitted to Texas Air Control Board, Mar. 19, 1976.

2. W. D. Bruce, IT Enviroscience, Inc., Trip Report to Nipro, Inc., Augusta, GA, Apr. 18, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. W. D. Bruce, IT Enviroscience, Inc., Trip Report to Allied Chemical Co., Hopewell, VA, Feb. 21, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

APPENDIX A

Table A-1. Physical Properties of Caprolactam[a,b]

Synonyms	Cyclic lactam, 2-aza-cycloheptanone, 6-aminohexanoic acid, aminocaprotic lactam
Molecular formula	$C_6H_{11}NO$
Molecular weight	113.16
Physical state	Solid
Vapor pressure	800 Pa at 120°C (6 mm Hg)
Boiling point	139°C at 1.60 kPa
Melting point	69-71°C
Liquid specific gravity	1.02 at 75°C/4°C
Water solubility	Soluble

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[a] J. Dorigan, B. Fuller, and R. Duffy, "Caprolactam," p. AI-210 in Scoring of Organic Dry Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C), MTR-7248, Rev. 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

[b] P. G. Stecher, Ed., The Merck Index, 8th ed., Merck and Company, Inc., p 202 (1968).

APPENDIX B

EXISTING PLANT CONSIDERATIONS

Table B-1. Emission Control Devices in Current Use

	Control Devices Used by		
Emission Source	Allied Chemical[a] Hopewell, VA	Badische Co.[b] Freeport, TX	Nipro, Inc.[c] Augusta, GA
Cyclohexanone purification	Condenser	Condenser	Closed system
Dehydrogenation reactor	Not applicable	Scrubber and incineration	Used as fuel
Oximation reactor and separator	None	None	None
Rearrangement	None	None	None
Neutralization reactor	Condenser	Condenser	No data
Phase separation, solvent recovery, and stripping	Condensers	Condenser	No data
Caprolactum purification	Scrubber, dust collector	None	None
Ammonium sulfate drying[d]	None	None	None
Ammonium sulfate cooling, screening, storage, and loading[d]	None	None	None

[a] See refs 1 and 2.

[b] See ref 3.

[c] See ref 4.

[d] Water scrubbers needed for ammonium sulfate recovery are part of the process and are not considered to be a control device.

Table B-1[1]—[4] lists process control devices reported in use by industry. As is described in the table, most of the control devices currently used by industry are the same control devices used to reduce the uncontrolled emissions from the conventional-process model plant.

Variations of the process for production of caprolactam are possible (see Sect. III). Some of these variations influence the amount and rate of the emissions. For example, in the neutralization reactor, toluene instead of benzene is added for extraction of the caprolactam. Such variations and the resulting influence on emissions should be considered before it is decided to retrofit control devices into existing plants. The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

---

[1] W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Allied Chemical Company, Hopewell, VA, Feb. 21, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

[2] F. L. Piguet, Allied Chemical, Hopewell, VA, letter dated Sept. 28, 1979, to D. R. Patrick (EPA).

[3] Badische Company emissions data on cyclohexanol/cyclohexanone and caprolactam production facilities supplied in response to EPA-114 letter request, May 12, 1978.

[4] W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Nitro, Inc., Augusta, GA, Apr. 18, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

REPORT 7

ADIPIC ACID

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Research Triangle Park, North Carolina

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Adipic acid production was selected for study because preliminary estimates indicated that volatile organic compounds (VOC) and adipic acid particulate emissions were significant. Also, although not of primary interest in this study, significant NO_x emissions are generated.[1]

Adipic acid is a white crystalline solid at ambient conditions; however, the product may be stored or transferred in either solid or molten form. Other pertinent physical property data are given in Appendix A.

B. USAGE AND GROWTH

Table II-1 gives a breakdown of domestic adipic acid consumption. The predominant end use of adipic acid is in the manufacture of nylon 6,6.[2] Other applications include plasticizers, synthetic lubricants, polyurethane resins, polyester resins, and food additives.[3]

It is estimated that adipic acid production will grow through 1981 at the rate of 4 to 5% per year, or somewhat less than the growth of nylon 6,6. A lower growth rate for adipic acid, compared with that of nylon 6,6, can be partly attributed to a shift in the use of raw materials for hexamethylenediamine (HMDA) production, which can be based on precursors other than adipic acid. (HMDA and adipic acid are co-monomers used in the production of nylon 6,6.)[4]

Another factor affecting the growth of adipic acid is the availability of cyclohexane, the primary raw material used in its production, which is obtained primarily by benzene hydrogenation. In 1974 cyclohexane-derived adipic acid production dropped 5 to 6% due to shortages of cyclohexane.[4]

C. DOMESTIC PRODUCERS

As of mid-1978 four manufacturers were producing adipic acid in a total of five plants; other pertinent data are given in Table II-2 and are shown in Fig. II-1.[2,4]

Table II-1. Domestic Adipic Acid Consumption[a]

End Use	Production (%)
Nylon fibers and plastics	90.0
Esters for plasticizers	4.0
Polyurethane resins	4.5
Miscellaneous[b]	1.5

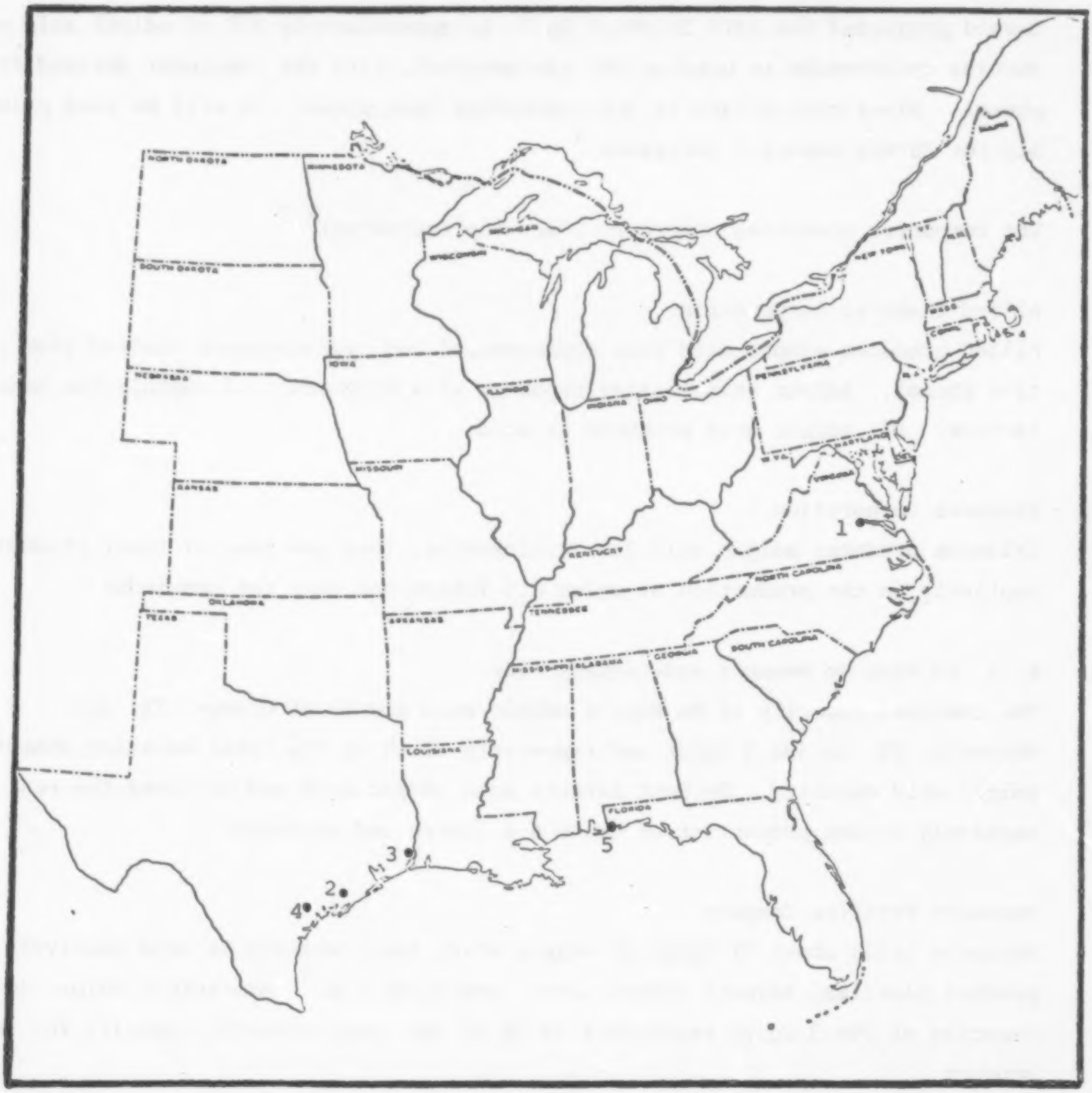
[a] See ref 3.

[b] Includes use of adipic acid in food additives, polyester resins, lubricants, etc.

Table II-2. Adipic Acid Capacity[a]

Company and Plant Location	Capacity (Gg/yr) as of February 1978	Basic Raw Material
Allied Chemical, Hopewell, VA	13.6	Phenol
Celanese, Bay City, TX	63.5	Cyclohexane
Du Pont, Orange, TX	181.4	Cyclohexane
Du Pont, Victoria, TX	317.5	Cyclohexane
Monsanto Textiles, Pensacola, FL	290.3	Cyclohexane
	866.3	

[a] See refs 3 and 4.


NORTH DAKOTA
MINNESOTA
SOUTH DAKOTA
WISCONSIN
MICHIGAN
NEW YORK
MASS
CONN
IOWA
NEBRASKA
ILLINOIS
INDIANA
OHIO
PENNSYLVANIA
MARYLAND
W. VA.
VIRGINIA
MISSOURI
KANSAS
KENTUCKY
NORTH CAROLINA
TENNESSEE
OKLAHOMA
TEXAS
ARKANSAS
SOUTH CAROLINA
GEORGIA
ALABAMA
MISSISSIPPI
LOUISIANA
FLORIDA
1
2
3
4
5

(1) Allied Chemical Corp., Hopewell, VA
(2) Celanese Chemical Co., Bay City, TX
(3) Du Pont Co., Orange, TX
(4) Du Pont Co., Victoria, TX
(5) Monsanto Textiles Co., Pensacola, FL

Fig. II-1. Location of Plants Manufacturing Adipic Acid

The overall domestic capacity for adipic acid is currently 866.3 Gg/yr,[2] and the demand projected for 1979 is 805.1 Gg.[3] In approximately 95% of adipic acid production cyclohexane is used as the raw material, with the remainder derived from phenol. Since cyclohexane is less expensive than phenol, it will be used primarily for future capacity increases.[4]

The companies producing adipic acid are the following:[2,3]

1. Allied Chemical Corporation
   Allied produces adipic acid from cyclohexanol and cyclohexanone derived from captive phenol. Adipic acid is also produced as a by-product of caprolactam manufacture. All adipic acid produced is sold.

2. Celanese Corporation
   Celanese produces adipic acid from cyclohexane; they use some of their product captively in the production of nylon 6,6 fibers and sell the remainder.

3. E. I. Du Pont de Nemours and Company, Inc.
   The combined capacity of Du Pont's adipic acid plants at Orange, TX, and Victoria, TX, is 498.9 Gg/yr and represents 57.6% of the total existing domestic adipic acid capacity. Du Pont markets some adipic acid and utilizes the rest captively in the production of nylon 6,6 fibers and plastics.

4. Monsanto Textiles Company
   Monsanto sells about 27 Gg/yr of adipic acid; the remainder is used captively to produce plastics, adipate plasticizers, and nylon 6.6.[5] Monsanto's adipic acid capacity of 290.3 Gg/yr represents 33.5% of the total domestic capacity for the product.

D. REFERENCES*

1. D. F. Durocher et al., Screening Study to Determine Need for Standards of Performance for New Adipic Acid Plants, GCA-TR-76-16-G, GCA Corp., Bedford, MA (July 1976).

2. "Chemical Profile on Adipic Acid," p 9 in Chemical Marketing Reporter, Feb. 20, 1978.

3. K. L. Ring et al., "CEH Marketing Research Report. Adipic Acid," pp 608.5031A—608.50330 in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1980).

4. J. L. Blackford, "CEH Marketing Research Report on Cyclohexane," p 638.5062K in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (February 1977).

5. Monsanto Textiles Co., letter dated June 11, 1979, to David R. Patrick (EPA).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

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III. PROCESS DESCRIPTIONS

A. INTRODUCTION

Starting with cyclohexane as the basic raw material, several synthesis routes to adipic acid are possible. The route used by all adipic acid producers except Allied Chemical is a liquid-phase, catalytic air oxidation of cyclohexane to yield cyclohexanol and cyclohexanone (KA oil). This is followed by nitric acid oxidation, with ammonium metavanadate and cupric nitrate used as catalysts, to obtain adipic acid.[1] The primary variation among producers is the catalyst they use in the cyclohexane oxidation step. Allied makes cyclohexanol by catalytic hydrogenation of phenol; however, the second step of adipic acid synthesis is basically the same as that used by the other producers. Although the phenol process for adipic acid is simple and produces fewer by-products, cyclohexane-based processes are preferred, largely because of the lower cost of cyclohexane.[1]

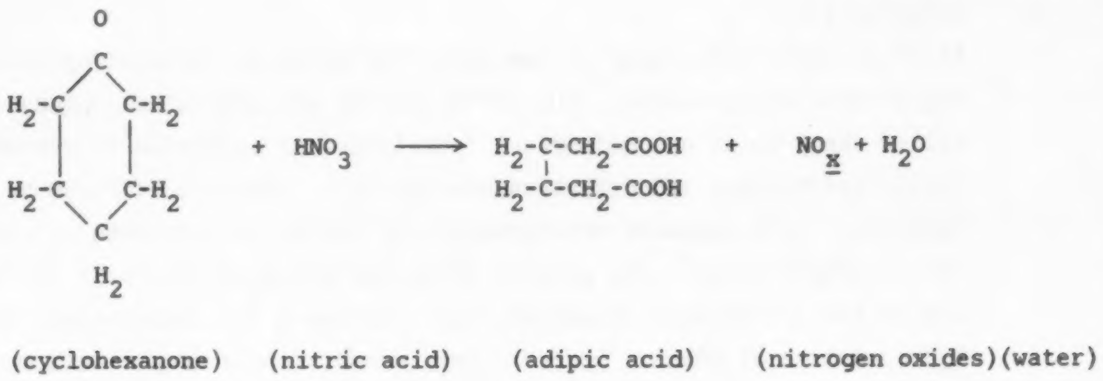
An alternate route for synthesizing adipic acid from cyclohexane (I. G. Farben process) involves two air oxidation steps: cyclohexane is oxidized to cyclohexanol and cyclohexanone; cyclohexanone and cyclohexanol are then oxidized to adipic acid, with a mixed manganese-barium acetate used as the catalyst.[1] Another possible synthesis method is a direct one-stage air oxidation of cyclohexane to adipic acid with a cobaltous acetate catalyst.[2] Cyclohexane can be oxidized all the way to adipic acid with nitric acid, but the yield is low and the process requires a large quantity of nitric acid.[1]

B. NITRIC ACID OXIDATION PROCESS

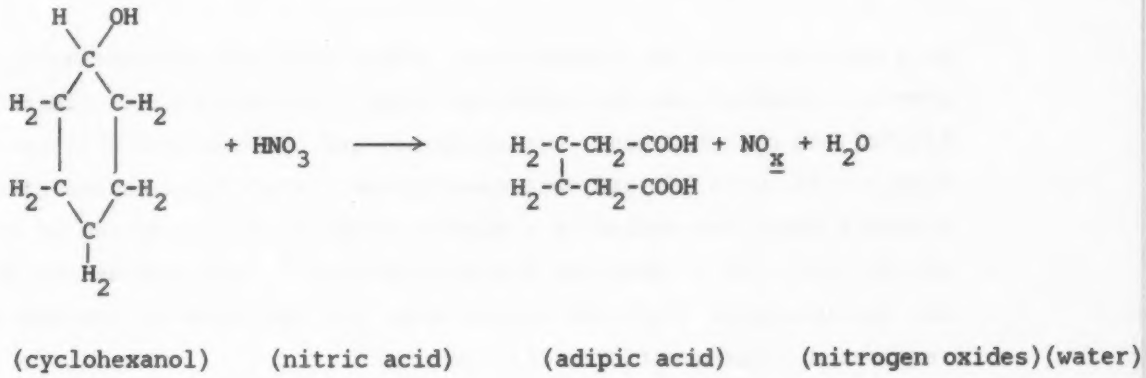
1. Basic Process

All adipic acid plants currently utilize basically the same process. Cyclohexanol or cyclohexanone or a mixture of the two (KA oil) is oxidized with nitric acid in the presence of a catalyst. Chemical reactions with cyclohexanol and cyclohexanone may be described[3] as follows (the reactions are not balanced):

Reaction 1:


O
C
H2-C
C-H2
H2-C
C-H2
C
H2
+ HNO3
H2-C-CH2-COOH
H2-C-CH2-COOH
+
NOx + H2O
(cyclohexanone)
(nitric acid)
(adipic acid)
(nitrogen oxides)(water)

Reaction 2:


H
OH
C
H2-C
C-H2
H2-C
C-H2
C
H2
+ HNO3
H2-C-CH2-COOH + NOx + H2O
H2-C-CH2-COOH
(cyclohexanol)
(nitric acid)
(adipic acid)
(nitrogen oxides)(water)

The nitrogen oxides generated by the reactions are nitric oxide, nitrogen dioxide, and nitrous oxide. Some organic by-products are also generated, such as glutaric acid, formic acid, acetic acid, and succinic acid.[3]

Figure III-1 is a flow diagram illustrating the basic process for adipic acid manufacture.[3,4] Production of adipic acid begins with a two-stage oxidation of cyclohexanol or cyclohexanone or a mixture of the two (KA oil) with a 50 wt % nitric acid solution. The catalysts (cupric nitrate and ammonium metavanadate) are dissolved in the acid solution. Optimum catalyst concentrations in the acid are about 0.25% copper and 0.1% vanadium.[4]

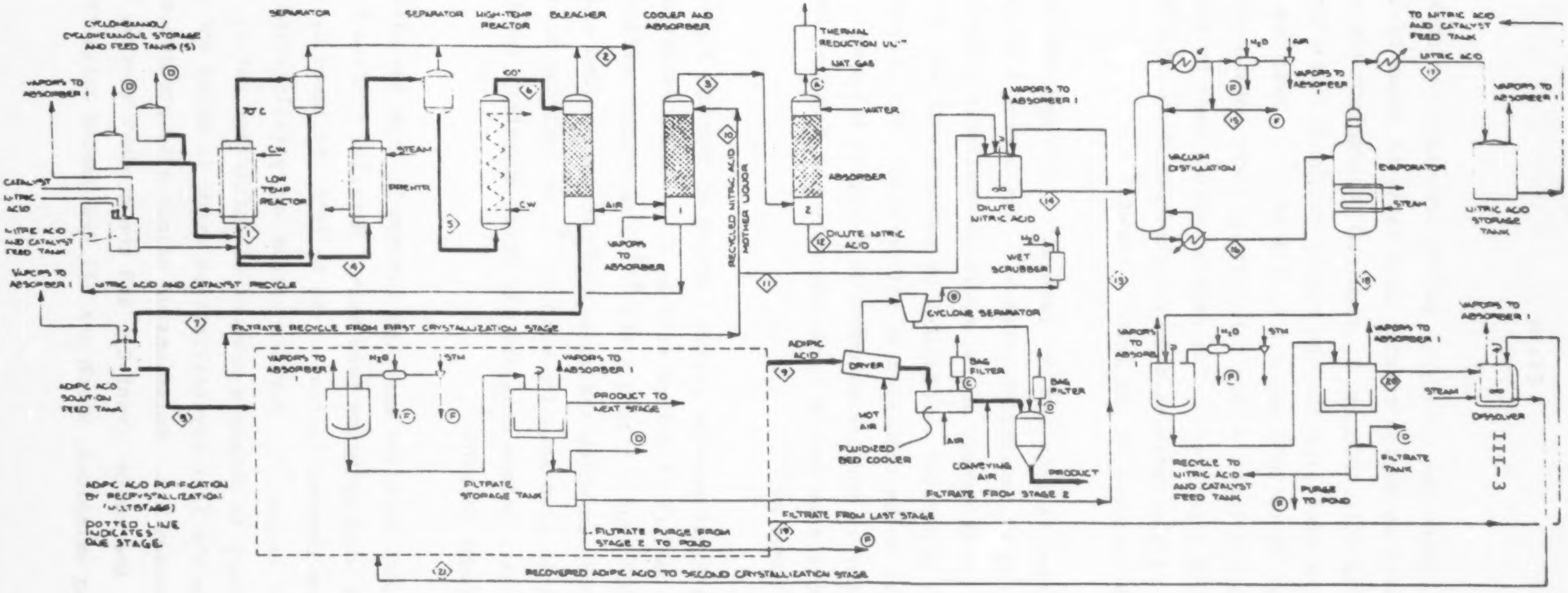

CYCLOHEXANOL/
CYCLOHEXANONE STORAGE
AND FEED TANKS (5)
VAPORS TO
ABSORBER I
D
CATALYST
NITRIC
ACID
NITRIC ACID
AND CATALYST
FEED TANK
VAPORS TO
ABSORBER I
NITRIC ACID AND CATALYST RECYCLE
SEPARATOR
70° C
CW
LOW
TEMP
REACTOR
1
SEPARATOR
STEAM
PREHTR
4
HIGH-TEMP
REACTOR
100°
6
CW
5
BLEACHER
AIR
2
COOLER AND
ABSORBER
1
VAPORS
TO
ABSORBER
3
10
RECYCLED NITRIC ACID
MOTHER LIQUOR
11
THERMAL
REDUCTION UNIT
NAT GAS
6
WATER
ABSORBER
2
12
DILUTE NITRIC
ACID
7
FILTRATE RECYCLE FROM FIRST CRYSTALLIZATION STAGE
ADIPIC ACID
SOLUTION
FEED TANK
8
VAPORS TO
ABSORBER I
H_2O
STM
F
VAPORS TO
ABSORBER I
PRODUCT TO
NEXT STAGE
FILTRATE
STORAGE TANK
FILTRATE PURGE FROM
STAGE 2 TO POND
ADIPIC ACID PURIFICATION
BY RECRYSTALLIZATION
(MULTISTAGE)
DOTTED LINE
INDICATES
ONE STAGE
21
RECOVERED ADIPIC ACID TO SECOND CRYSTALLIZATION STAGE
VAPORS TO
ABSORBER I
DILUTE
NITRIC ACID
14
H_2O
WET
SCRUBBER
13
ADIPIC
ACID
9
DRYER
HOT
AIR
FLUIDIZED
BED COOLER
AIR
B
CYCLONE SEPARATOR
BAG
FILTER
C
BAG
FILTER
CONVEYING
AIR
PRODUCT
FILTRATE FROM STAGE 2
FILTRATE FROM LAST STAGE
19
VACUUM
DISTILLATION
H_2O
AIR
VAPORS TO
ABSORBER
I
15
16
EVAPORATOR
STEAM
NITRIC ACID
17
TO NITRIC ACID
AND CATALYST
FEED TANK
VAPORS TO
ABSORBER I
NITRIC ACID
STORAGE
TANK
18
VAPORS
TO
ABSORB
I
STM
20
FILTRATE
TANK
RECYCLE TO
NITRIC ACID
AND CATALYST
FEED TANK
PURGE
TO POND
STEAM
DISSOLVER

Fig. III-1. Process Flow Diagram for Manufacture of Adipic Acid by Nitric Acid Oxidation Process in Model Plant

The nitric acid (containing the catalyst) and cyclohexanol-cyclohexanone streams (1) are fed to the first oxidation reactor in a ratio of about 40:1.[4] The high concentration of nitric acid solution is required to complete the oxidation and to provide a sufficient heat sink for the highly exothermic reaction.[4,5] The reactor is operated at 70 to 80°C and 0.1 to 0.4 MPa.[4,5] Reactors for the oxidation either are stirred tanks or are circulating loops having a pump, heat exchanger, and gas-liquid separator.[5] The reactor volume must be sufficient for about 90% conversion of the cyclohexanol-cyclohexanone feed, and the surface area must be sufficient for removal of the reaction heat.[4]

The gas-liquid separator is required for removal of nitrogen and the nitrogen oxides that emerge from the oxidation process.[5] The presence of nitrogen oxides (hence nitrous acid) is necessary for a smooth controllable reaction.[4] The nitrogen oxide from the separator is oxidized by contact with air and enters (stream 2) an absorber to be recovered as nitric acid. The effluent (stream 3) from the first absorber is further scrubbed in a second absorber. Nitrogen and water vapor, along with some nitric oxide and nitrogen dioxide, from the second absorber are vented (vent A).[4,5]

The product from the first reactor passes (stream 4) through a preheater and a gas-liquid separator before it enters (stream 5) a second oxidation reactor operated at about 100°C and 0.1 to 0.4 MPa.[4,5] The reactor effluent (stream 6) then enters a bleacher, in which the dissolved nitrogen oxides are stripped from the adipic acid—nitric acid solution with air.[4] In addition to acting as the stripping agent the air, before entering the first absorber, further oxidizes nitric oxide to nitrogen dioxide.[4]

The adipic acid product solution emerging (stream 7) from the bleacher is collected in the adipic acid solution feed tank. Material (stream 8) from the feed tank undergoes vacuum crystallization at 30 to 70°C, followed by centrifugation to remove the mother liquor.[3,5] Further vacuum recrystallization of adipic acid from water is necessary to obtain a product of sufficient purity.[4] Wet adipic acid (stream 9) from the last crystallization stage is dried and cooled and then transferred to a storage bin. Emissions of adipic acid particulates occur from the dryer (vent B), the cooler (vent C), and the product storage bin (grouped with storage and handling emissions, which are all designated collectively with the letter D).

The mother liquor from the first crystallization step is recycled (stream 10) to the first absorption tower.[4] The mother-liquor stream (11) is continually purged to a system for removal of other dibasic acids (primarily succinic and glutaric) and for recovery of residual adipic acid, nitric acid, and catalysts.[4,5] Various schemes have been developed for recovery of residual adipic acid, nitric acid, and catalysts.

One representative recovery scheme is to combine the dilute nitric acid (stream 12) from the second absorber, the mother liquor (containing nitric acid) (stream 13) from the second crystallization stage, and a purge stream (11) of mother liquor from the first crystallization stage and process them for recovery of nitric acid, adipic acid, and catalysts. The combined acid (stream 14) is vacuum-distilled for water removal (stream 15) and recovery of nitric acid (stream 16) at approximately its azeotropic concentration in water. Stream 16 is sent to an evaporator for further removal of the liquid phase. The overhead product (nitric acid) (stream 17) from the evaporator is transferred to a storage tank, and the bottom product (stream 18) from the evaporator is sent to a vacuum crystallizer for recovery of adipic acid. A portion of the filtrate from the centrifuge is taken for purging the system of dibasic acids. The remainder is recycled to the nitric acid and catalyst feed tank.

The filtrate (stream 19) from the last crystallization stage is utilized for dissolution (stream 20) of the recovered adipic acid. The recovered adipic acid solution (stream 21) is recycled to the second crystallization stage.

2. Process Variations (Fig. III-1)

In some processes bleacher effluent (stream 7) is concentrated by vacuum stripping to remove water and monobasic acids (e.g., acetic acid). The bottoms from the still are vacuum-crystallized for recovery of product adipic acid. The mother liquor is recycled for use in the oxidation reactors. These variations will not affect process emissions since vapors are routed to absorber No. 1.

Buildup of dibasic acids, such as succinic and glutaric, is controlled by a portion of the mother liquor being continually purged to a system for recovery of the nitric acid, most of the adipic acid, and the catalyst.[4]

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In Fig. III-1 stream 9 leaves the crystallization section and passes to a dryer and a cooler and then to a storage bin. In some cases crystallization may be followed by a heater to melt the adipic acid for storage in a molten state, especially if it is to be used on-site.[3]

C. REFERENCES*

1. M. E. O'Leary, "CEH Marketing Research Report on Adipic Acid," pp 608.5032A—C in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA, January 1974.

2. K. Tanaka, "Adipic Acid by Single Stage," Hydrocarbon Processing 55(11), 114—119 (1974).

3. D. F. Durocher et al., Screening Study to Determine Need for Standards of Performance for New Adipic Acid Plants, GCA-TR-76-16-G, GCA Corp., Bedford, MA (July 1976).

4. McKetta and Cunningham, Encyclopedia of Chemical Processing and Design, vol 2, pp. 129—146, Dekker Publishing Co., New York, 1971.

5. D. E. Danly and C. R. Campbell, "Adipic Acid," pp 510—531 in Kirk-Othmer Encyclopedia of Chemical Technology, 3d ed., vol 1, edited by M. Grayson et al., Wiley-Interscience, New York, 1978.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. MODEL PLANT FOR NITRIC ACID OXIDATION OF CYCLOHEXANOL/CYCLOHEXANONE

The model plant* for this study has a capacity of 150 Gg/yr based on 8760 hr** of operation annually and represents the approximate average capacity of the single process train used by major domestic adipic acid producers. The process of nitric acid oxidation of cyclohexanol and cyclohexanone represents current adipic acid manufacturing and engineering technology.

Typical raw-material and product-storage-tank capacities were estimated for a 150-Gg/yr plant. Storage tank requirements are discussed under Sect. B-4. Characteristics of the model plant that are important in atmospheric- dispersion modeling are given in Appendix B. Emission considerations for existing plants are given in Appendix D.

B. SOURCES AND EMISSIONS

1. General

Emissions from the model plant are classified as process, storage and handling, secondary, and fugitive emissions. Process and secondary emissions from the model plant are based on data obtained from plant-site visits and reports submitted to the EPA.[1,2] Storage emissions were estimated with equations in AP-42.[3] Fugitive emissions were determined by estimating the number of pumps, process valves, and pressure-relief valves for each unit operation and multiplying by the appropriate factors given in Appendix C.

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*See p I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly production rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will normally operate on the same cycle as the process. Therefore from the standpoint of cost effectiveness calculations the error introduced by assuming continuous operation is negligible.

Emission rates and sources associated with the adipic acid model plant are listed in Table IV-1. For each source the emissions are broken down into volatile organic compounds (VOC) and particulates. For vent A (see Fig. III-1) only, NO_x emissions are listed since a data base is readily available and since they occur simultaneously with the VOC emissions.

2. Process Emissions

Process emissions occur from absorber No. 2, the adipic acid dryer, and the adipic acid cooler (vents A, B, and C, Fig. III-1). Emissions from vent A are composed of volatile organic compounds and nitrogen oxides. Organic emissions from vent A are normally low because of a large excess of nitric acid, which is required in the oxidation reactor to provide a heat sink for the exothermic reaction and to drive the reaction to completion. To some extent monobasic carboxylic acid by-products, such as acetic acid, leave with the oxidation reactor off-gases and go to the absorbers. Small quantities of these compounds exit through vent A.

Process upsets causing a rapid increase in cyclohexanol and cyclohexanone emissions from the oxidation reactors may cause an increase in VOC emissions from vent A, even though oxidation of the organics by nitric acid solution occurs to some extent in the absorbers. Hydrocarbon emissions are not increased during shutdowns, because the cyclohexanol-cyclohexanone feed is stopped at the beginning of the shutdown procedure.

Drying and cooling of the adipic acid product create particulate emissions from vents B and C. According to actual process data particulate emissions are the most significant uncontrolled emissions in the process.[1,2] Process upsets, startups, and shutdowns affect the particulate emission rate to the extent that they affect the rate of product processed through the dryer and product cooler.

3. Fugitive Emissions

Process pumps and valves are potential sources of fugitive emissions. The model plant is estimated to have 56 pumps (28 of which are spares) handling VOC. The

Table IV-1. Model-Plant Uncontrolled Emissions

Emission Source	Vent or Emission Designation (Fig. III-1)	Uncontrolled Emissions					
		Ratio[a] (kg/kg)			Rate (kg/hr)		
		VOC	Adipic Acid Particulate[b]	NO_x	Total VOC	Adipic Acid Particulate[b]	NO_x
Absorber No. 2	A	2.01×10^{-4}		4.74×10^{-2}	3.44		811
Adipic acid drying	B		7.94×10^{-4}			13.6	
Adipic acid cooler	C		7.83×10^{-2}			1340.0	
Storage and handling	D	5.0×10^{-5}	7.30×10^{-2}		0.86	1250.0	
Fugitive	E	8.3×10^{-5}			1.42		
Secondary[c]	F						

[a] kg of emission per kg of adipic acid produced.

[b] Even though particulates prior to filtration are classified with uncontrolled emissions, a bag filter is normally used to prevent product loss. The bag filter could logically be considered a necessary part of the process equipment, thereby essentially eliminating this uncontrolled emission.

[c] Emissions are less than 1 Mg/yr and are considered to be negligible.

estimated number of process valves is 349, and the number of pressure-relief valves is 22. The fugitive emission factors for heavy-liquid service shown in Appendix C were applied to this valve and pump count to determine the fugitive emissions given in Table IV-1.

4. Storage and Handling Emissions

VOC emissions result from storage and handling of cyclohexanol-cyclohexanone. For the model plant the storage emission sources are shown on the flow diagram in Fig. III-1 (source D). The model-plant storage tanks are listed in Table IV-2.

Since cyclohexanol-cyclohexanone storage tanks in the adipic acid process are the primary source of VOC storage emissions, storage-tank emission calculations were based on cyclohexanol-cyclohexanone. Estimates of KA oil storage tank sizes, turnovers per year, and bulk liquid temperature were influenced by the data given in EPA reports.[4—7] Emissions listed in Table IV-1 for these storage tanks are based on fixed-roof tanks, half full, and a 10°C diurnal temperature change. Equations from AP-42[3] were used for the calculations. However, breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing loss equation overestimates emissions.[8]

Particulate emissions resulting from transfer of adipic acid to a storage bin were determined for the model plant from data given for an existing process, and are included in Table IV-1.[2]

5. Secondary Emissions

In the model plant, secondary emissions occur only from aqueous effluent discharged from the plant. The effluent is transferred by pipeline to a holding pond and is then sent to deep well or by pipeline. The total aqueous effluent is estimated to be 230 Mg/day. Of this, 59 Mg/day is nonvolatile organic acids, such as succinic, glutaric, and adipic acid; 47 Mg/hr is nitric acid; and the remainder is water.

To evaluate the significance of secondary organic emissions from the holding pond, a hypothetical worst-case situation was devised. It was assumed that the aqueous stream is composed of 25% succinic acid, the most volatile organic acid in the stream, and that the remainder is water. A closed system, ideal solution, and

Table IV-2. Model-Plant Storage-Tank Data[a]

Process Segment	Tank Contents	No. of Tanks Required (Fig. III-1)	Tank Size (m^3)	Turnovers per Year	Bulk Temperature (°C)[b]
KA oil feed	Cyclohexanol, cyclohexanone, misc. hydrocarbons	1	80.2	200	65
		1	80.2	1500	88
		2	80.2	Constant level	65
		1	258	Constant level	65
Nitric acid and catalyst feed[c]	Nitric acid, organic acids, water	1	568.9	377	31
Adipic acid product storage bin[c]	Adipic acid, product	1	1135.0	182	49
Adipic acid solution feed to product still[c]	Adipic acid, nitric acid, misc. organic acids, water	1			
Adipic acid solution feed to crystallizers[c]	Adipic acid, nitric acid, misc. organic acids, water	1			
Centrifuge filtrate storage[c]	Nitric acid, misc. organic acids, water	4			
Dilute nitric acid storage[c]	Nitric acid, misc. organic acids, water	1			
Nitric acid storage (after evaporator)[c]	Nitric acid, water	1			

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[a] Cyclohexanol-cyclohexanone storage is considered as part of the adipic acid process rather than as a part of the precursive process.

[b] Temperatures based on reported data (ref 5); bulk temperatures could be lower, which would reduce VOC emissions.

[c] Although emissions from these segments are less than 1 Mg/yr and are considered to be negligible, they are included because the tanks contain some organic material; tank parameter data incomplete.

ideal gas in equilibrium with the aqueous solution were also assumed. With these assumptions the mole fraction of succinic acid in the vapor phase is 2.0×10^{-8} (or 20 ppb by volume).

Additional calculations were performed in which a Henry's-law constant was estimated for the vapor-liquid system and was compared with information given in an article by Thibodeaux.[9] Following this line of reasoning secondary VOC emissions resulting from the wastewater stream were estimated to be less than 1 ton/yr. It was then estimated that secondary emissions are negligible compared with other emissions of organic compounds from the model plant.

C. REFERENCES*

1. W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Monsanto Textiles Company, Pensacola, FL, Feb. 8, 1978 (data on file at EPA, ESED, Research Triangle Park, NC).

2. D. R. Durocher *et al*., Screening Study to Determine Need for Standards of Performance for New Adipic Acid Plants, GCA-TR-76-16-G, GCA Corp., Bedford, MA (July 1976).

3. C. C. Masser, "Storage of Petroleum Liquids," pp 4.3-1—4.3-16 in Compilation of Air Pollutant Emission Factors, AP-42, 3d ed. (August 1977).

4. Response by Monsanto Textiles, Pensacola, FL, to EPA questionnaire on adipic acid, Air Pollution Control Engineering and Cost Study of the Petrochemical Industry, OMB Approval No. 158 S 72019 (Aug. 31, 1972).

5. Response by Celanese Chemical Co., Bay City, TX, to EPA questionnaire on adipic acid, *ibid*. (Aug. 15, 1972).

6. Response by Du Pont, Orange City, TX, to EPA questionnaire on adipic acid, *ibid*. (Sept. 18, 1972).

7. J. M. Mullins, Celanese Chemical Co., Bay City, TX, Texas Air Control Board 1975 Emissions Inventory Questionnaire (July 9, 1976).

8. E. C. Pulaski, TRW, letter dated May 30, 1979, to Richard Burr (EPA).

9. L. J. Thibodeaux, "Air Stripping of Organics from Wastewater. A Compendium," pp 358—378 in The Proceedings of the Second National Conference on Complete Watereuse. Water's Interface with Energy, Air and Solids, Chicago, IL, May 4—8, 1975, sponsored by AIChE and EPA Technology Transfer.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. PROCESS SOURCES

Process emissions from the model plant occur from vents A, B, and C. Vent A emits both NO_x and volatile organic carbon compounds; vents B and C emit adipic acid particulate matter. (See Fig. III-1 for vent locations and Table IV-1 for uncontrolled emissions.)

Emissions from vent A can be controlled with a thermal reduction unit, by a scrubber, by combustion in a boiler, or by flaring. A recent study[1] by the GCA Corporation indicates that thermal reduction is the best proven means for control of NO_x emissions from adipic acid plants. Efficiency of NO_x removal for this type of device is about 97% but varies with the inlet NO_x concentration. Thermal reduction units can take any inlet concentration of NO_x and reduce the outlet NO_x concentration to about 500 ppm by volume, even at high flow rates. The Monsanto plant is presently running its thermal reduction unit at 1500 ppm because of problems with the ceramic liner cracking but it has been run at 500 ppm. Comments in the GCA report[1] concerning the effectiveness of combustion techniques for removal of hydrocarbons indicate that VOC emissions from vent A can be removed with almost 100% efficiency in a thermal reduction unit; this value was used for calculation of model-plant VOC emissions from vent A (see Table V-1). The control devices currently used by adipic acid producers is shown in Appendix D.

In the thermal reduction unit, off-gases containing nitrogen oxides are heated to high temperatures and reacted with excess fuel (natural gas) in a reducing atmosphere. Three steps are involved in this process: At ~2600°F nitrogen oxides are reacted with excess fuel under reducing conditions to form water vapor, elemental nitrogen, and carbon dioxide; the gases are cooled to 1400°F by a heat recovery unit; and the excess fuel is combusted, usually in the presence of a catalyst.[1]

Scrubbers are used in industry for NO_x emissions control, but the lower achievable concentration limit with the best available systems is approximately 1000 ppm (by volume). For removal of low concentrations of NO_x (less than 1 vol %) at high flow rates, NO_x removal efficiency is about 70%. In some adipic acid plants NO_x emissions are routed to a powerhouse boiler, a combustion technique similar to thermal oxidation. In the GCA report this technique is estimated to be about 70%

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Table V-1. Model-Plant Controlled Emissions

Type of Emission	Emission Source	Vent or Emission Designation (Fig. III-1)	Control Device or Technique	Controlled Emissions						
				Emission Reduction (%)	Emission Rate (kg/hr)			Emission Ratio (kg/kg/)[a]		
					VOC	Par-ticulate	NO_x	VOC	Par-ticulates	NO_x
Process	Absorber No. 2	A	Thermal reduction unit	98 NO_x; 100 VOC			16.4			9.56×10^{-4}
Process	Adipic acid dryer	B	Wet scrubber	79.5		2.79			1.63×10^{-4}	
Process	Adipic acid cooler	C	Bag filter	99.98		0.27			1.57×10^{-5}	
Storage and handling	Storage tanks or bins	D	Floating roofs on KA stg. tanks	85 VOC	0.12	0.55		7.5×10^{-6}	3.20×10^{-5}	
			Bag filter on adipic acid stg. bin	99.96 Part.						
Fugitive	Pumps, valves, pressure-relief valves	E	Detection and correction of major leaks		1.42			8.3×10^{-5}		
Secondary[b]	Holding pond	F	None							
Totals					1.54	3.61	16.4	9.1×10^{-5}	2.11×10^{-4}	9.56×10^{-4}

[a] kg of emission per kg of adipic acid produced.

[b] Emissions are less than 1 Mg/yr and are considered to be negligible.

efficient for removal of NO_x. The use of flares is also reported, but they are only about 70% efficient for the removal of NO_x.[1]

Removal of VOC from the stream leaving vent A with the scrubber, used for removal of NO_x, would be inefficient since water is used as the scrubbing solvent, and cyclohexanol, cyclohexanone, and cyclohexane have low water solubilities. If a boiler or a flare is used for NO_x removal, about 99% VOC reduction is achievable.

Emissions from vents B and C are adipic acid particulates from the dryer and product cooler, respectively, which are controlled industrially by wet scrubbers and/or bag filters. The typical efficiency of bag filters for the removal of particulates is greater than 99%, provided that the relative humidity of the stream is low. High relative humidity results in caking and consequent operating problems with the filters. The use of bag filters on humid air streams necessitates heating the stream or diluting it with relatively dry air to prevent caking and related problems. In contrast the efficiency of a wet scrubber may range from about 80 to 95%, depending on its design, but there are no potential operational problems from caking or from high-energy consumption to prevent condensation. Model-plant controlled emissions from the dryer are based on data for a wet scrubber with about 80% particulate removal efficiency. Model-plant controlled emissions from the dryer product stream are based on a bag filter with a particulate removal efficiency of 99.98%.[1]

B. FUGITIVE SOURCES

Controls for fugitive sources will be discussed in a separate document covering fugitive emissions from the synthetic organic chemicals manufacturing industry. Controlled fugitive emissions calculated with the factors given in Appendix C are included in Table V-1. These factors are based on the assumption that any major leaks will be detected and repaired.

C. STORAGE AND HANDLING SOURCES

Controls for storage emissions are discussed in another EPA document.[2] Control for VOC storage losses involves the use of new, floating-roof tanks,* or other appropriate control devices. The VOC storage emissions listed in Table V-1 for

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*Consist of internal floating covers or covered floating roofs as defined in API 25-19, 2d ed., 1976 (fixed-roof tanks with internal floating device to reduce vapor loss).

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the model plant were calculated by assuming that 85% control can be provided by a contact type of internal floating roof with secondary seals. If the storage temperature were reduced to about 40°C, the need for a contact type of internal floating roof may be eliminated.

An alternative technique (not currently employed) for controlling VOC storage emissions in the adipic acid model plant consists of routing them to the thermal reduction unit. Combustion of the hydrocarbons would virtually eliminate VOC storage emissions but would not have the advantage of recovery offered by floating- roof tanks.

Emissions of adipic acid particulates result from the product storage bin. In the model plant a bag filter is used to control particulate emissions from the bin. A particulate removal efficiency of 99.96% was used for calculation of the controlled emissions given in Table V-1.[1]

D. SECONDARY SOURCES

Aqueous effluent from the adipic acid manufacturing process contains dibasic organic acids, such as adipic, succinic, and glutaric.[3,4] Since these compounds are essentially nonvolatile, air emissions resulting from an aqueous solution of them are insignificant, and no control device or technique is considered to be necessary for VOC control.

E. REFERENCES*

1. D. F. Durocher _et al_., _Screening Study to Determine Need for Standards of Performance for New Adipic Acid Plants_, GCA-TR-76-16-G, GCA Corp., Bedford, MA (July 1976).

2. D. G. Erikson, IT Enviroscience, Inc., _Storage and Handling_ (in preparation for EPA, ESED, Research Triangle Park, NC).

3. W. D. Bruce, IT Enviroscience, Inc., _Trip Report for Visit to Monsanto Textiles Company, Pensacola, FL, Feb. 8, 1978_ (data on file at EPA, ESED, Research Triangle Park, NC).

4. Response by Monsanto Textiles Co., Pensacola, FL, to EPA questionnaires on adipic acid, _Control Engineering and Cost Study of the Petrochemical Industry_, OMB Approval No. 158 S 72019 (Aug. 31, 1972).

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VI. IMPACT ANALYSIS

A. CONTROL COST IMPACT

This section gives the cost considerations for control of VOC emissions resulting from the production of adipic acid. Details of the model plant (Fig. III-1) are covered in Sects. III and IV.

1. Absorber No. 2—Vent A

A thermal reduction unit for NO_x control can also be used for elimination of VOC emissions, such as those that occur from vent A, Fig. III-1, of the model adipic acid plant. With a thermal reduction unit already in existence for NO_x control no additional cost is incurred for VOC control. Consequently, cost-effectiveness calculations for VOC removal are unnecessary.

2. Cyclone Separator Vent and Fluidized-Bed Cooler Vent (Vents B and C, Fig. III-1)

Emissions from vents B and C are entirely adipic acid particulates and are not regarded as VOC emissions. The same is true for the vent on the adipic acid product storage bin, located just after the fluidized bed cooler. For economic reasons adipic acid plants employ control devices on these vents, and the control devices are considered to be an integral part of the process. For the reasons indicated in Sect. 1 cost-effectiveness calculations were not performed for the bag filters on those vent streams.

3. Storage and Handling

Model-plant cyclohexanol-cyclohexanone storage emissions are controlled by the use of floating-roof tanks. Installed capital cost, net annual cost, and cost-effectiveness data are contained in another EPA report covering storage of chemicals.

b. Fugitive Sources—A control system for fugitive sources is defined in Appendix C. Another document will cover fugitive emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.

c. Secondary Sources—No control system has been identified for the secondary emissions from the model plant.

B. ENVIRONMENTAL AND ENERGY IMPACTS

Control of emissions from storage tanks is achieved through the use of floating-roof tanks, which do not consume energy and have no adverse energy or environmental impacts.

Control of fugitive emissions is achieved by the prompt correction of leaks on pumps, agitators, and compressors. These control techniques do not have adverse energy or environmental impacts.

Use of a thermal reduction unit for NO_x and VOC, of floating-roof storage tanks, and of fugitive-emission control techniques results in a VOC emissions reduction of 36.6 Mg/yr for the model plant.

VII. SUMMARY

Adipic acid is currently produced exclusively from nitric acid oxidation of cyclohexanol and cyclohexanone. Other synthesis routes to adipic acid are feasible, such as two-stage air oxidation from cyclohexane, but are not now being utilized industrially.[1]

The annual growth rate of adipic acid through 1981 is estimated to be 4 to 5%. As indicated in Sect. II, the current capacity for adipic acid is 866.3 Gg/yr, and the demand for 1979 is projected to be 805.1 Gg/yr. Slight capacity increases by process modifications will be required for increased production capacity, with the projected demand assumed to be accurate. If growth continues to increase at the projected rate, some plant expansions will be required.

About 90% of the adipic acid manufactured is used in the production of nylon 6,6 fibers and plastics. Consequently, growth of adipic acid is strongly dependent on the demand for nylon 6,6. Availability of basic raw materials, such as cyclohexane and phenol, can also be influential economic factors.[2]

Emission sources and control levels for the adipic acid model plant are summarized in Table VII-1. The predominant VOC emissions points in the model plant are from absorber No. 2 (vent A), fugitive sources (i.e., pumps, valves, and pressure-relief valves), and storage tank sources. Projection of these emission values for the entire domestic adipic acid industry at the estimated 1979 demand would result in VOC emissions of 30.7 kg/hr for all uncontrolled plants. It is estimated that VOC emissions from the adipic acid industry are currently 73% controlled. The estimated current emission rate of VOC, based on the projected product demand for 1979, is 8.3 kg/hr.

With model-plant process VOC emissions assumed to be controlled in existing equipment used for NO_x control and fugitive emissions to be controlled by increased

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[1] M. E. O'Leary, "CEH Marketing Research Report on Adipic Acid," pp 608.5032A—K in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (January 1974).

[2] J. L. Blackford, "CEH Marketing Research Report on Cyclohexane," p 638.5062K in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (February 1977).

Table VII-1. Model-Plant Emission Summary[a]

	Emission Rate (kg/hr)					
	Uncontrolled			Controlled		
Emission Source	VOC	NO_x	Particulate	VOC	NO_x	Particulate
Absorber No. 2	3.44	811			16.4	
Adipic acid dryer			13.6			2.79
Adipic acid cooler			1340			0.27
Storage and handling	0.86		1250	0.12		0.55
Fugitive	0.86			0.86		
Total	5.16	811	2600	0.98	16.4	3.61

[a] All emissions are based on a plant operation rate of 8760 hr/yr; secondary emissions are less than 1 Mg/yr and are considered to be negligible.

maintenance, the only additional significant VOC emissions to be controlled are storage emissions. Cyclohexanol-cyclohexanone storage is controlled in the model plant by floating-roof tanks, which would allow an overall VOC emission reduction of approximately 85% to be attained.

APPENDIX A

Table A-1. Physical Properties of Adipic Acid[a]

Synonyms	Hexaneodioic acid, adipinic acid, 1,4-butane-dicarboxylic acid
Molecular formula	$C_6H_{10}O_4$
Molecular weight	146.14
Physical state	White, crystalline solid
Vapor pressure	133 Pa at 159.5°C
Vapor density	5.04 (air = 1)
Boiling point	337.5°C
Melting point	153°C
Density	1.360 at 25°C[b]
Water solubility	Slight (15 g/liter)

[a] J. Dorigan, B. Fuller, and R. Duffy, p Al-42 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A--C), MTR-7248, Rev. 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

[b] With reference to water at 4°C.

Table A-2. Physical Properties of Cyclohexanone[a]

Synonyms	Ketohexamethylene, cyclohexylketone , pimelic ketone, hexanon
Molecular weight	98.14
Physical state	Liquid
Vapor pressure	4.77 mm at 25°C
Vapor density	3.4 (air = 1)
Boiling point	155.6°C
Melting point	-47°C
Density	0.9478 at 20°C[b]
Water solubility	50g/liter

[a] J. Dorigan, B. Fuller, and R. Duffy, p AI-322 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A--C), MTR-7248, Rev. 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

[b] With reference to water at 4°C.

Table A-3. Physical Properties of Cyclohexanol[a]

Synonyms	Hexahydrophenol, hexalin
Molecular weight	100.17
Physical state	Liquid
Vapor pressure	1.7 mm at 25°C
Vapor density	3.45 (air = 1)
Boiling point	161.5°C
Melting point	23°C
Density	0.9449 at 25°C[b]
Water solubility	Yes

[a] J. Dorigan, B. Fuller, and R. Duffy, p AI-320 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A--C), MTR-7248, Rev. 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

[b] With reference to water at 4°C.

Table A-4. Physical Properties of Cyclohexane[a]

Synonyms	Hexahydrobenzene, hexanaphthene, hexamethylene
Molecular weight	84.16
Physical state	Liquid
Vapor pressure	98.14 at 25°C
Vapor density	2.90 (air = 1)
Boiling point	80.7°C
Melting point	6.3°C
Density	0.77855 at 20°C[b]
Water solubility	Insoluble (<1g/liter)

[a] J. Dorigan, B. Fuller, and R. Duffy, p AI-318 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A--C), MRT-7248, Rev. 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

[b] With reference to water at 4°C.

APPENDIX B

Table B-1. Atmospheric-Dispersion Parameters for Adipic Acid Model Plant (Capacity, 150 Gg/yr), Controlled and Uncontrolled

Emission Source	Emission Rate (g/sec)	Tank Height (m)	Tank Diameter (m)	Stack Height (m)	Stack Diameter (m)	Discharge Temperature (K)	Flow rate (m^3/sec)	Discharge Velocity (m/sec)
Uncontrolled Emissions								
Process absorber vent A (Fig. III-1)	57.3			30	1.05	330		
Cyclohexanol/ cyclohexanone storage tanks (5)								
1	1.24	4.9	4.6			338		
2	12.50	4.9	4.6			361		
3	0.13	4.9	4.6			338		
4	0.13	4.9	4.6			338		
5	0.33	7.3	6.7			338		
Fugitive	23.7					310--375		
Controlled Emissions								
Process absorber vent A (Fig. III-1)				30	1.05	533	8.64	10
Cyclohexanol/ cyclohexanone storage tanks (5)								
1	0.19	4.9	4.6			338		
2	1.88	4.9	4.6			361		
3	0.02	4.9	4.6			338		
4	0.02	4.9	4.6			338		
5	0.05	7.3	6.7			338		
Fugitive	23.7					310--375		

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

EXISTING PLANT CONSIDERATIONS

Table D-1[1,2] lists process control devices reported in use by industry. Most of them are the same control devices used to reduce the uncontrolled emissions from the process model plant.

The largest source of uncontrolled VOC emission is from absorber No. 2 (vent A); however, the NO_x reductions from the vent also result in reduction of VOC emissions. In the model plant it was assumed that a thermal reduction unit could be used to reduce NO_x emission, as well as VOC emissions. A thermal reduction unit is currently being used by Monsanto and was designed to reduce NO_x emissions to 500 ppm. The Monsanto unit is presently running at 1500 ppm NO_x because of problems with the ceramic liner cracking, but it can and has been run at 500 ppm. At the lower NO_x concentrations (500 ppm) the unit will be down one-half the time because of thermal cracking, whereas if the unit runs at 2500 ppm NO_x, then it will be operating almost full time.[1] In Du Pont's plants powerhouse boilers are used to reduce NO_x emissions to the 2500—5000 ppm range. The boilers are designed to provide steam, to operate while the adipic acid process is in operation, and to recover most of the energy value of their fuel. The thermal reduction unit wastes most of the supplemental fuel's energy value because it has no provision for heat recovery or the waste heat recovery unit is not as efficient as a boiler.[3]

Celanese states that in a properly designed and operated plant with a high-pressure absorber there should be essentially no volatile organic emission from the adsorber. Three reasons are given: there is essentially total conversion of the volatile organics in the reactor, the reactor off-gas is scrubbed by

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[1] D. F. Durocher *et al.*, *Screening Study to Determine Need for Standards of Performance for New Adipic Acid Plants*, GCA-TR-76-16-G, GCA Corp., Bedford, MA (July 1976).

[2] F. L. Piguet, Allied Chemical, Hopewell, VA, letter dated June 29, 1979, to D. R. Patrick (EPA).

[3] J. R. Cooper, Du Pont, Wilmington, DE, letter dated July 24, 1979, to D. R. Patrick (EPA).

Table D-1. Emission Control Devices Used by Adipic Acid Producers[a]

Company	Vent A Absorber Number 2			Vent B Dryer Control Device	Vent C Cooler Control Device
	Control Device	NO_x Reduction (%)	VOC Reduction (%)		
Allied Chemical	[b]			Wet scrubber	Not applicable
Celanese	[c]				
Du Pont, Orange, TX	Powerhouse[d]	70	99	Wet scrubber	Bag filter
Du Pont, Victoria, TX	Powerhouse	70	99	Bag filter	Bag filter
Monsanto	Thermal reduction unit	97	99+	Wet scrubber	Wet scrubber

[a] See refs 1 and 2.

[b] Absorber off-gas routed to caprolactam process; no NO_x emission.

[c] Efficiency of nitric acid recovery section ∿95%; no further NO_x control required.

[d] Absorber off-gas routed to powerhouse, which also burns waste gases from other processes.

incoming blend acid feed, and the reactor off-gas is further scrubbed in a high-pressure absorber.[4]

As is described in Sect. III of this report, variation of the process for the production of adipic acid is possible. Some of these variations, for example, in the design and operation of the reaction off-gas scrubbers, influence the amount and rate of the emissions. Such variations and resulting influence on emissions should be considered before it is decided to retrofit control devices into existing plants.

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

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[4] Celanese Chemical Company, Bay City, TX, letter dated June 25, 1979, to D. R. Patrick (EPA).